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A Characterization and Evaluation of Coal Liquefaction Process Streams

Quarterly Technical Progress Report
April 1 through June 30, 1995

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EXECUTIVE SUMMARY

HTI RUN CMSL-8

Analyses by standard and non-standard analytical techniques were completed on 27 process samples from representative periods of HTI Run CMSL-8 in which Illinois 6 bituminous coal and coal/plastics were the feedstocks. The analytical results provide information on the chemical transformation of these feedstocks and their distribution in product and recycle streams, and have implications for coal/plastic co-liquefaction processing and for analysis of samples from these processes. Several unusual process oil characteristics were observed when plastics were coprocessed with coal. The major conclusions from characterization of Run CMSL-8 samples are listed below.

- Polystyrene (PS) products are identifiable and quantifiable in the separator overhead (SOH) distillate product from coal/mixed plastics co-liquefaction. With the in-line hydrotreater operating, approximately 50% of the PS fed to the process can be accounted for as the alkylbenzene products ethylbenzene and cumene.

- High-density polyethylene (HDPE) appears to be an important source of n-paraffins in the separator overheads (SOHs) and heavy distillates from coal/plastics co-liquefaction.

- The SOH sample from period 9 in which the in-line hydrotreater was by-passed was much poorer in quality than the SOHs produced with the hydrotreater in operation.

- Identification of some PS and polyethylene terephthalate (PET) products in the SOHs may be masked by highly effective in-line hydrotreating. Addition of a hydrotreater feed sample point to the plant or of more off-line hydrotreater reference periods to future run plans may help in identification of plastics liquefaction components in the SOHs.

- Incompletely converted HDPE constituted 15 to 30 wt % of the pressure-filter liquid (PFL) recycle streams, and was found as tetrahydrofuran (THF)

insolubles; virtually no THF insolubles were present in the PFL from the coal-only period. THF insolubility is currently the best way to separate unconverted HPDE in liquid samples which contain no other solids.

- Phase separation in some PFL distillation resids indicates that HDPE products have complex phase behavior.

- Upper limits for both single-pass and overall conversions of HDPE during Run CMSL-8 were estimated. It was assumed that: 1) the HTI unit was operating at steady-state, 2) that the PFL THF-insolubles are unconverted HDPE, and 3) that there was no unconverted HDPE in the pressure-filter cake (PFC). During Run CMSL-8, PFL was both the recycle liquid and a liquid product. HDPE conversions were estimated to be ca. 80% overall, and ca. 25% single-pass, and the conversions were responsive to changes in process conditions.

- Fourier-transform infrared (FTIR) spectroscopy is useful for the identification of HDPE products.

- Field-ionization mass spectrometry (FIMS) allows distinction of coal-derived material and HDPE-derived material in process stream samples. Quantification of HDPE appears to be possible using the FIMS technique, but additional development is needed.

RESID REACTIVITY

A conference call with the University of Delaware was held on April 26, 1995, to discuss analytical requirements for the kinetic modeling work. A record of the call is attached as Appendix 4.

The solids portion of twenty-nine reaction products from experiments performed in Delaware's STBR were received for analysis. Ultimate analyses and ash elemental analyses were completed. Results of the analysis will provide the basis for selecting catalyst and reaction conditions for the next phase of work with a variety of resid samples.

Arrangements were made with Western Research Institute to analyze the 15 samples in the University of Delaware sample set by CP/MAS ^{13}C-NMR.

Delaware's quarterly report for this reporting period is attached as Appendix 3.

NOVEL ANALYTICAL TECHNIQUES

West Virginia University (WVU) performed a single exploratory experiment in the high pressure/high temperature electron spin resonance (ESR) cell with a coal liquid resid. Based on results of this test and recommendations made at the conclusion of a previous project conducted under DOE Contract DE-AC22-89PC89883 with WVU, we will pursue a possible subcontracted project

TECHNOLOGY TRANSFER

A paper, "Caustic Washing for Refining of Direct Coal Liquefaction Products", was accepted for presentation at the 210th Annual Meeting of the American Chemical Society, in August 1995, in Chicago, IL, in the symposium "Direct Coal Liquefaction". The paper is authored by R. A. Winschel, P.-Z. Zhou (BRSC), F. P. Burke, G. A. Robbins, and S. D. Brandes. The written preprint is included as Appendix 5 in this report.

An invited paper, "Characteristics of Process Oils from HTI Coal/Plastics Co-Liquefaction Runs", was prepared for presentation at the Ninth Annual CFFLS Technical Meeting, August 15-18, in Pipestem, WV, and the 1995 DOE Coal Liquefaction and Gas Conversion Contractors Review Conference, August 29-31, 1995, in Pittsburgh. The paper is authored by G. A. Robbins, S. D. Brandes, R. A. Winschel, and F. P. Burke. The written preprint as submitted to the DOE conference is included as Appendix 6 in this report. The abstract as submitted to the CFFLS conference is included as Appendix 7 in this report.

A paper was accepted for presentation at the 210th Annual Meeting of the American Chemical Society entitled "A Novel Method for the Determination of the Boiling Range of Liquid Fuels by Thermogravimetric Analysis", by He Huang, Keyu Wang, Shaojie Wang, M. T. Klein, and W. H. Calkins. The preprint is included as Appendix 8 of this report.

A paper, "The Role of Process Oil Characterization in Direct Coal Liquefaction" was accepted for presentation at the Twelfth Annual International Pittsburgh Coal Conference, "Pittsburgh, PA, September 11-15, 1995. The paper is authored by F. P. Burke and R. A. Winschel. The written paper is included as Appendix 9 in this report.

Section 2
INTRODUCTION

This is the Technical Progress Report for the fourth quarter of activities under DOE Contract No. DE-AC22-94PC93054. It covers the period April 1 through June 30, 1995.

CONTRACT OVERVIEW

The objectives of this project are to support the DOE direct coal liquefaction process development program and to improve the useful application of analytical chemistry to direct coal liquefaction process development. This project will build on work performed in DOE Contract No. DE-AC22-89PC89883. Independent analyses by well-established methods will be obtained of samples produced in direct coal liquefaction processes under evaluation by DOE. Additionally, analytical instruments and techniques which are currently underutilized for the purpose of examining coal-derived samples will be evaluated. The data obtained from this study will be used to help guide current process development and to develop an improved data base on coal and coal liquids properties. A sample bank will be established and maintained for use in this project and will be available for use by other researchers. The reactivity of the non-distillable resids toward hydrocracking at liquefaction conditions (i.e., resid reactivity) will be examined. From the literature and data experimentally obtained, a mathematical kinetic model of resid conversion will be constructed. It is anticipated that such a model will provide insights useful for improving process performance and thus the economics of direct coal liquefaction.

CONTRACT ACTIVITIES THIS QUARTER

- Analyses were completed on 27 process samples from representative periods of HTI Run CMSL-8 in which Illinois 6 bituminous coal and coal/plastics were the feedstocks. The analytical results reported here provide information on the chemical transformation of these feedstocks and their distribution in product and recycle streams. The characteristics of the products and process streams were dependent on both feedstock changes and operating conditions. Several unusual process oil characteristics were observed when plastics were coprocessed with coal. Implications of these

results for future coal/plastics liquefaction development and analytical characterization of the materials are discussed.

- Recommendations for DOE's accelerated development program in coal/waste co-liquefaction were provided to the PETC project team.

- A request was made to HTI for samples from the coal liquefaction bench-unit Run CMSL-10, which was conducted during this report period. The sample request is included as Appendix 1 of this report.

- We have been asked by DOE to act as a clearinghouse for samples from HTI Run CMSL-9. HTI has supplied sufficient sample to us for further distribution to other research groups, e.g., the Consortium for Fossil Fuel Liquefaction Science (CFFLS). A list of available samples was provided to DOE/PETC and to CFFLS.

- We began and completed some of the analyses on the 81 samples received from HTI bench-scale Run CMSL-9, in which coal, coal/mixed plastics, and coal/HDPE were fed. Additional analytical work on these samples will continue next quarter.

- A conference call with the University of Delaware was held on April 26, 1995, to discuss analytical requirements for the kinetic modeling work. A record of the call is appended to this report. Prior to this conference call, Delaware indicated to us the analytical data they want to have to support the kinetic modeling work. They have no need for characterization of the products, only the feedstocks. The characterization data they require includes proton NMR data, carbon NMR data (structural parameters are desirable but aromaticity would suffice), C, H, N, S analysis, -OH determinations, simdist (to quantify any distillables in the feedstocks), and molecular weight determinations (such as by VPO or FIMS) on SARA fractions of the feeds. They also are interested in sulfur and nitrogen speciation. This list of analytical needs was discussed further, and priorities for analyses were set during the conference call.

- Liquid chromatographic separation of the fifteen resid samples in the Delaware set was started this quarter. A separation scheme which produces four fractions (saturates, aromatics, resins, and asphaltenes) was requested by Delaware because of their previous experience with the data produced by this scheme for kinetic modeling. It is anticipated that all fifteen samples will be analyzed by the end of the next quarter.

- Four papers were authored or co-authored by CONSOL researchers, and are appended to this report. One paper, authored by University of Delaware researchers, also is appended.

ACTIVITIES IN PROGRESS

- Analyses are being conducted on samples received from HTI bench-scale Run CMSL-9. Analytical work will continue into the next quarter. Run CMSL-9 samples will be distributed to other research groups on request.

- A full set of samples was requested from HTI Run CMSL-10 (Appendix 1). After they are received, samples will be distributed to other research groups on request. No timetable has been established for analysis of these samples, although it is expected to follow or overlap analysis of the Run CMSL-9 samples.

- A statement of work for Western Research Institute (WRI) was drafted for analysis by CP/MAS ^{13}C-NMR spectroscopy of 15 coal-derived resid samples. These samples comprise the total set of resid samples which the University of Delaware is investigating in their subcontract. We sent WRI a single sample to examine before issuing a cost quote.

- Dr. M. Seehra of West Virginia University (WVU) performed a single exploratory experiment in the high pressure/high temperature ESR cell with a coal liquid resid (Wilsonville Run 257 V131B). The results of that test conducted at 1000 psi (static) H_2 at temperatures from ambient to 450 °C indicate that there is a significant decrease in free radical concentration above 100 °C. WVU sent us data from this single exploratory experiment. Based on these data and recommendations made at the conclusion of a

previous project conducted under DOE Contract DE-AC22-89PC89883 with WVU, we will pursue a possible subcontracted project.

- Conoco inspection tests of HTI POC-1 and POC-2 net products still are ongoing.

Section 3
RESULTS AND DISCUSSION

HTI RUN CMSL-8

HTI Run CMSL-8 Background

A diagram of HTI's bench unit 227 as configured for Run CMSL-8 (also known as Run 227-85) is shown in Figure 1.[1] CONSOL analyzed samples from sample points 3 through 7, representing recycle and product streams; feed samples had been previously analyzed.[2,3,4] Samples were also obtained from sample point 1, but were not analyzed. The operating conditions and process performance summary for the run are given in Table 1.[1] The feed during Run CMSL-8 was 100 wt % coal, or coal with 25 wt % to 33 wt % plastic (mixed or HDPE). The feed coal was from the Crown II Mine, Illinois 6 seam. The feed plastics consisted of HDPE or a mixture of high density polyethylene/polystyrene/polyethylene terephthalate (HDPE/PS/PET) in the proportion 50/35/15. HTI's feed analyses are given in Table 2. The temperature configuration was low/high. Supported catalyst was present in the first liquefaction reactor only; dispersed Fe/Mo catalyst also was added to the first reactor. An in-line fixed-bed reactor was used to hydrotreat the light distillate product oil. The start-up solvent was the same petroleum-derived oil used during Run POC-2 operations;[1,2] its analysis is shown in Table 3.

In Run CMSL-8, HTI found:[1]

1. With plastics in the feed, the light gas yield and H consumption were lower at the same level of total conversion and distillate yield.

2. HDPE was harder to convert to 975 °F$^-$ material than coal or other plastics.

3. Plastics, especially HDPE, require a more severe depolymerization/cracking environment than Illinois 6 coal.

4. In-line hydrotreating was very effective for producing distillate with less than 10 ppm each of S and N.

Operating performance was good early in the run, but as the run continued, the resid conversion decreased. Increasing catalyst age and three increases in the

concentration of polyethylene in the feed were believed to contribute to decreasing resid conversion.[1] Several adjustments were made to other process conditions after period 16 to maintain performance and operability. These and other significant events were: the change from coal-only operation in periods 1-6 to 75% coal and 25% mixed plastics in periods 7-11 and 12-16; the increase in second-stage reactor temperature from 830 to 850 °F and an increase in first-stage space velocity from 30 to 40 lb dry feed/hr/ft^3 reactor in periods 12-16; the increase in mixed plastics concentration to 33% in periods 21-23 and a decrease in space velocity from 40 to 30 lb dry feed/hr/ft^3 reactor from period 18 on, and an increase in dispersed Mo catalyst concentration from 100 to 200 ppm, from period 19 on; and, in periods 21-23, the switch from 33% mixed plastics to 33% HDPE. Over the duration of the run, the supported catalyst reached an age of 966 lb dry feed/lb cat. Samples received as either period 22 or period 23 samples were considered to represent material balance period 22.

Prior Run Background and Current Analytical Objectives

CONSOL previously analyzed process stream samples from coal-only and coal/waste portions of HTI Run POC-2, although steady-state operation was not achieved during these brief periods. Some results obtained from characterization of samples from Run POC-2 coal/plastics operation are:[2,3] (1) Polystyrene (PS) products were identified and quantified in distillate product oil. (2) Incompletely converted high-density polyethylene (HDPE) was found as tetrahydrofuran (THF)-insoluble material in the ash-free-resid recycle stream. It was unclear to what extent this material was present in the ROSE bottoms stream. Unusual solubility behavior seems to be associated with HDPE-derived material in resid-containing streams. The broad implication is that HDPE was difficult to convert at the operating conditions used. (3) The unusual presence of a product-oil sediment raised questions about the stability of the product oil. (4) Analytical issues were identified including how to identify and quantify HDPE, the appropriateness of applying coal liquefaction work-up procedures to coal/plastics liquefaction, and how to measure the extent of plastics liquefaction.

Along with the analytical difficulties, the brevity of the coal/plastics liquefaction period in Run POC-2 prevented these issues from being resolved. To better evaluate these issues, the major portion of Run CMSL-8 was performed with coal/plastics feed. The two runs were very different, e.g., CMSL-8 was performed

at a smaller scale and over a longer period than Run POC-2. Other differences included reactor configuration, temperatures, and feed coal. Most importantly, the plant operated in solvent balance, which did not occur during the coal/plastics portion of Run POC-2. Solvent-balanced operation in Run CMSL-8 meant that samples, material balances, and performance results from Run CMSL-8 were representative of operation with the coal/plastics feedstocks. Coal/HDPE liquefaction was tested in Run CMSL-8, in addition to coal/mixed plastics liquefaction. The results from characterization of Run CMSL-8 process oil samples are presented below.

Specific analytical objectives of this work are to determine:

- the fate of the plastics feedstocks, relative to coal-only operation
- the conversion of the feedstocks
- interactions of feedstocks
- how the use of plastics feedstocks affects product quality
- to what degree oil property differences reflect feedstock differences vs. other (process) condition changes, such as unit operations, space velocity, and catalyst age

Analyses Performed

A brief description of the Run CMSL-8 samples and analyses conducted as CONSOL's baseline characterization is provided in Table 4. In this report, the samples will be referred to by the abbreviations given in Table 4, e.g., SOH for the product oil, PFL for the recycle liquid, and PFC for the bottoms stream. The baseline analytical methods can be applied to many different kinds of samples, can be performed quickly, and have proven to be suitable for liquefaction process stream characterization. In addition to the routine laboratory analyses, non-routine characterization (such as FTIR characterization of certain samples) was performed, based on the Run POC-2 sample experience. Several samples were selected for specialized analyses, such as plasma desorption mass spectrometry (PDMS) and field ionization mass spectrometry (FIMS).

CONSOL received and analyzed 27 process stream samples from Run CMSL-8. In the analytical scheme summary given in Table 4, sample points, SP-xx, correspond to those shown in Figure 1. Most samples were received in 1-quart or 1-gallon cans; SOH and ASOH samples were received in 1-quart plastic bottles. Also received from

Run CMSL-8, but not analyzed, were feed slurry samples, SP-1. Some SOH samples consisted of two phases. Each lower phase was found to be water and contained only minor amounts of hydrocarbon. Therefore, it was omitted from the analytical data tables, and the results reported are only from the upper phase.

Each whole SOH and ASOH oil sample was analyzed by ^{1}H-NMR (Table 7) for proton distribution and by FTIR for phenolic -OH content (Table 10). Proton distributions were obtained by ^{1}H-NMR for the pyridine-soluble portion of PFL, PFC, and CAS bottoms whole samples (Table 7). The PFL and CAS bottoms whole samples were distilled (Table 5) to 320 °C pot/270 °C column/5 torr (850 °F/atm). The pyridine-soluble portion of each 850 °F$^+$ resid was analyzed by ^{1}H-NMR (Table 9). The 850 °F$^+$ distillation bottoms samples were extracted with tetrahydrofuran (Table 5). Each THF-soluble extract was analyzed by solubility fractionation (Table 6) and by FTIR for phenolic -OH content (Table 10). From each THF-insoluble filter cake a sample was ashed, and the insoluble organic matter (IOM, also called unconverted coal, or UC) content was calculated by difference (Table 5). Each 850 °F$^-$ distillate was analyzed by ^{1}H-NMR (Table 8) and FTIR (Table 10).

Microautoclave tests were made at the modified equilibrium conditions (9 g solvent, 6 g standard coal, 750 °F, 30 min) with selected whole samples and their 850 °F$^-$ distillates (Table 11). Microautoclave coal conversions were calculated with a correction for solids in the oils.

Whole PFL, PFC, and CAS bottoms samples were extracted with tetrahydrofuran (THF) (Table 5). Each THF-soluble extract was analyzed by solubility fractionation (Table 6) and by FTIR for phenolic -OH content (Table 10). From each THF-insoluble filter cake a sample was ashed, and the insoluble organic matter content was calculated by difference. Selected THF insoluble filter cakes were inspected for HDPE using FTIR spectroscopy.

Overview of Run Results

CONSOL has an ongoing effort to improve the analytical capabilities for analysis of materials produced from coal/plastics co-liquefaction. However, some characteristics, as measured by our routine techniques, of specific process streams which are presented in Tables 5-11 and Figures 2-14 seem to show complicated or inconsistent responses to run conditions. This may reflect either the complexity

of the chemistry, or some inappropriateness of the analytical techniques, or both.

Some notable characteristics or observations made from our work with these samples, some based on routine techniques, others based on specialized non-routine analyses, are presented here.

There is concern about the integrity of three of the five CAS bottoms samples, since they were found to contain only traces of ash (Table 5, samples from periods 11, 20, and 23). HTI also reported[1] very low ash values for two of the three suspect samples (those from periods 11 and 20).

The concentration of the 850 °F$^-$ distillate in the PFL and CAS bottoms streams decreased as the run progressed (Table 5, Figure 2). Some portion of this decrease may be expected as the catalyst ages. A progressive increase in feed HDPE concentration with run period may also contribute to the decreasing distillate concentration. HTI observed increasing 975 °F$^+$ resid concentration in the PFL and increasing 975 °F$^+$ resid yield as the run progressed.[1] They attributed some of the increase to the HDPE feed.

THF insolubles in the PFL samples (Table 5) seem to contain primarily HDPE, as is discussed later.

PFC samples are consistent in the concentration of resid, IOM and ash after period 6 (Table 5). These data are in good agreement with those of HTI,[3] who by methods different from those of CONSOL found IOM concentrations to be 14.6 wt % (period 6) and 21.0 to 26.2 wt % (periods 11-23); and ash concentrations to be 43.3 to 45.7 wt % (all periods).

In general, during period 16, the overall quality of the PFL and its distillate and resid fractions was improved, relative to PFL quality during the other run periods. This was manifested in lower aromaticity, lower phenolic -OH concentration, and lower preasphaltene and asphaltene concentrations in the whole sample THF extract and resid THF extract (see Figures 3-7, Figures 9-13, and Tables 6-10). Conversely, the CAS bottoms quality seemed to worsen during this period, as observed in many of the same properties (Figures 3-6, Figures 8-13,

and Tables 6-10). Since the CAS bottoms stream is the feed to the filtration unit to produce the PFL and PFC streams, and the PFL is the major filtration product stream, the opposite trend in properties for the CAS bottoms and PFL streams seems unusual. These results make the period 16 CAS bottoms sample integrity suspect.

Some PFL and PFL distillate and resid fraction properties seem to worsen between periods 16 and 20, or between periods 20 and 23 (Figures 3-7, Figures 9-13, and Tables 6-10). Although the specific cause is not certain, run performance generally declined through the run as a result of catalyst aging and possibly because of the increase in feed HDPE concentration, which was the largest near the end of the run. It also is possible that HDPE concentration in the system built up over the course of the run.

Phenolic -OH concentration shows about the same trend through the run for every stream except the CAS bottoms (Figure 13, Table 10). The general trend was to increase in phenolic -OH through the run, except for a dip or plateau during period 16. In general, the highest phenolic -OH concentrations occurred near the end of the run. This may be caused primarily by catalyst deactivation effects. The temperature increase in period 16 appears to be responsible for temporarily lowering the phenolic concentration in most streams, but they subsequently increased after period 16.

Donor solvent quality of the whole PFLs, and PFL 850 °F$^-$ distillates, as measured by a standard microautoclave test, is shown in Figure 14, and given in Table 11. Whole PFL solvent quality was fair to poor at 71.5% in period 6, and very poor at 0 to 36.8% for all of the coal/plastics periods. PFL distillate solvent quality was poor to fair, ranging from 58.5 to 78.6%, and was lowest during period 16. The PFL distillate from the coal period was only slightly better in donor quality than the corresponding whole PFL, whereas in the samples from coal/plastics operations, the PFL distillates were significantly better donor solvents than their whole PFL counterparts. The poor donor quality of the whole PFLs produced from coal and plastics appears to result from the unreacted HDPE, which is not present in the 850 °F$^-$ distillate. This could result from poor donor ability of the HDPE and perhaps incompatibilities of liquid phase

components. HDPE is chemically related to n-paraffins, which are known to be non-donors in coal liquefaction.

SOH Product Characteristics and Effects of In-line Hydrotreating

The separator overheads (SOHs) from periods 6 and 11 through 23 were consistently low in aromatic hydrogen and high in paraffinic hydrogen content (Figure 15), relative to concentrations typically observed. There was no change in paraffinic hydrogen content of SOHs from period 6 (coal-only) to period 11 (coal/mixed plastics). However, a substantially lower paraffinic hydrogen content was observed when the in-line hydrotreater was by-passed in period 9. This indicates that, because of extensive upgrading in the hydrotreater, the paraffinic hydrogen content of the SOH may be relatively insensitive to other process changes. The product oil (SOH) sample and atmospheric still overhead (ASOH) sample from period 9, in which the in-line hydrotreater was by-passed, are much poorer in quality than the SOHs produced with the hydrotreater in place. Differences included medium brown in color vs. colorless, presence of a "coal liquid" odor, more aromatic, less paraffinic, and considerably higher phenolic -OH concentration (Figure 2). There was a small increase in paraffinic hydrogen in SOH samples from periods 16, 20, and 23, coincident with increases in the HDPE concentration in the feed (8.75, 11.5, and 33 wt % dry feed, respectively). The effects of hydrotreating on the SOH properties observed in this run were greater than those observed in Run POC-2.[2] This may be because the distillate hydrotreated in Run CMSL-8 is a thermal distillate, and the distillate of Run POC-2 came from a catalytic reactor.

Gas chromatography-mass spectrometry (GC-MS) total ion chromatograms of SOH samples (Figure 16) show that replacing a portion of the coal with mixed plastics in period 7 and the switch from mixed plastics to HDPE in period 21 increased the concentrations of n-paraffins in the SOHs, and shifted the n-paraffins to higher molecular weight. Thus, HDPE appears to be an important source of the n-paraffins in the SOHs produced after period 6. Two peaks corresponding to ethylbenzene and cumene (isopropylbenzene) are marked in Figure 16. These components are polystyrene (PS) liquefaction products. Cumene was not found in the coal-only period SOH, and ethylbenzene was present at about 1% concentration in the coal-only and coal/HDPE periods 6 and 23. ^{1}H-NMR results indicate that PS products persisted in the SOH product from the coal/HDPE period. In the NMR

spectra of the SOHs (Figure 17), ethylbenzene features are nonexistent in the coal period SOH, quite prominent in the coal/mixed plastics-period SOHs, and observable, but small, in the coal/HDPE-period SOH.

The PS products were quantified by GC-MS and ^{1}H-NMR (Table 12). The area of the ethylbenzene and cumene peaks, as a percentage of the total ion chromatogram was used to estimate the concentration of these components in the SOHs. The alkylbenzene concentration of the SOHs was estimated (as ethylbenzene) by integration of the ^{1}H-NMR peak near 7.1 ppm (see Figure 17). Based on these estimates, ethylbenzene and cumene constitute about 8-15 wt % of the coal/mixed plastic period SOHs (with the HTU in use), less than 1 wt % of the coal/HDPE period SOH, and about 2 wt % or less of the coal period SOH. When the hydrotreater was bypassed with the coal/mixed plastics feed, the concentration increased to about 15 to 23 wt % of the SOH. With the in-line hydrotreater operating, approximately 50% of the PS fed to the process can be accounted for as these alkylbenzene products.

HDPE Products in Heavy Distillate

The GC-MS total ion chromatograms of 850 °F$^-$ distillate from CAS bottoms stream samples are shown in Figure 18. It is evident that the coal-derived aromatic components are surpassed by n-paraffins in prominence when plastics are coliquefied with coal after period 6. As in the SOH samples, HDPE appears to be an important source of the n-paraffins in the 850 °F$^-$ distillate portions of the CAS bottom produced after period 6.

HDPE in Recycle and Resid Samples

The PFLs from the coal/plastics periods 11, 16, 20, and 22 contained 15 to 30 wt % THF insolubles. These insolubles were tan with white specks early in the run and dark brown later in the run. The presence of THF insolubles in the PFL is a unique feature of coal/plastics processing. PFLs from coal-only operations (including period 6 of this run) typically contain little or no THF-insoluble material. The FTIR spectra of insolubles from coal/plastics periods 11 and 22 were similar and indicated that they are polyethylene-like material (Figure 19). PFL 850 °F$^+$ distillation bottoms from two of three coal/mixed-plastics periods (periods 11 and 20) separated into two solid phases upon cooling; none of the other PFL resids behaved in this way. The two phases differed in physical

characteristics and color. The upper phase was lighter in color (brown, instead of black) and much less brittle than the lower phase. The upper phase constituted 66.7 wt % of the period 11 bottoms and 34.6 wt % of the period 20 bottoms. Diffuse reflectance FTIR (Figure 19) was used to examine both phases of the period 11 PFL distillation resid. The upper phase appeared to be predominantly plastic derived (much of it PE), and the lower phase is predominantly coal derived. The spectrum of the upper brown phase indicated primarily aliphatic hydrocarbons with PE-like features (sharp double peaks around 1470 and 720 cm^{-1}). Aromatic hydrocarbon peaks also were significant, but no features indicated the presence of heteroatomic functional groups. The spectrum of the lower black phase showed more intense aromatic hydrocarbon peaks than did the upper phase. It also showed peaks indicating a significant amount of aliphatic hydrocarbon, but no distinctive PE-like features. The spectrum of the lower phase also contains prominent peaks from heteroatomic functionality, perhaps N-H and O-H. Thus, the upper phase seems to represent a predominantly plastic-derived component (much of it PE), and the lower phase a predominantly coal-derived component. Neither phase completely dissolved in the pyridine-d_5 used for the ^{1}H-NMR analysis. We believe that it was primarily polyethylene products that were insoluble in the pyridine.

FIMS Analysis Results

Samples of both PFL Period 11 resid phases and five other samples (Period 22 PFC, PFL, PFL THF-insolubles, PFL THF-solubles, and HDPE) from Run CMSL-8 also were characterized by field-ionization mass spectrometry (FIMS) at SRI International.[5-7] The pyrolysis profiles are shown in Figures 20a-g and the FIMS spectra in Figures 20h-n. Volatilization of each sample from the instrument sample probe was nearly complete. The pyrolysis profiles show that HDPE begins to pyrolyze to low molecular weight components at about 430 °C and is completely evolved by 500 °C (Figure 20a), and that the THF-insoluble sample from the period 22 PFL exhibits similar behavior and is believed to be nearly all HDPE (Figure 20b). Other samples (Figure 20c-g) show nearly constant evolution of material from 25 °C to 500 °C. As such, any HDPE in these samples is not recognizable merely on the basis of the pyrolysis profile. In the mass spectra, the HDPE pyrolysis products are lower in molecular weight and generally distinct from the coal-derived resid components (Figure 20h-n). The HDPE and perhaps long-chain n-paraffins in the co-liquefaction samples produce a series of low-

mass ions separated by 14 Da, beginning with 57 Da, as seen in Figure 20h-n. Lower-mass peaks are not seen, because data collection was begun with mass 48 Da to eliminate contributions from lighter hydrocarbon gases. These spectra confirm the identification of the period 22 PFL THF insolubles as being nearly pure HDPE (Figure 20h-i), and show that HDPE is present in varying amounts in the other samples analyzed from coal/plastic operating periods (Figure 20j-n). The THF-soluble fraction of the period 22 PFL (Figure 20j) appears to contain only a small amount of HDPE. The PFL 11 resid plastic layer (Figure 20m) contains more HDPE than the corresponding coal layer (Figure 20n). Furthermore, the odd/even mass ratio is higher for the coal layer, suggesting that it contains more nitrogen heteroatomic species. This is consistent with the FTIR results presented in Figure 19.

There are no sensitivity factors readily available for relative quantification of HDPE-derived and coal-derived material. Low-mass ions from fragmentation of n-paraffins are usually seen as minor components in coal liquefaction products. Longer-chain ($\approx C_{30}$ or higher) paraffin waxes such as those found in Fischer-Tropsch wax fractions can thermally fragment in the FIMS to give 20 to 50% of the intensity in the low mass region of the spectrum of an F-T wax.[8] This high degree of fractionation also is expected for the HDPE, and, as was shown above, does occur under the conditions of the FIMS analysis. Therefore, it would not be possible to observe thermal fragment ions of paraffins distinctly from those of HDPE, but the contribution of low-mass ions from typical coal liquefaction products is small.[6,7] Thus, the low-mass peaks in the FIMS spectra appear to represent primarily HDPE-derived liquefaction products.

Two simple quantitation methods were tried with the FIMS M_N and M_W/M_N data (Table 13); for several samples the methods appear to work fairly well. In one approach, a linear relationship between the HDPE concentration and the number average molecular weight (M_N) determined by FIMS was assumed. A correction to the method is needed for samples containing distillate of molecular weight lower than 600 Da; whole PFL and the THF-soluble fraction of the PFL are two such samples. The data in Table 13 indicate that the polydispersity (M_W/M_N) determined from FIMS data is probably related to HDPE concentration, since the high polydispersity of about 3.6 is found in HDPE and in the THF insoluble sample, and the low polydispersity of about 1.2 is found in coal resid samples.

A linear relationship between the HDPE concentration and the polydispersity (M_W/M_N) determined from FIMS data was assumed. A distillate correction also may be necessary with this approach. The mathematical validity of both of these linear relationships has not been established; for the polydispersity approach, a non-linear relationship between wt % HDPE and polydispersity is probably more appropriate; only a linear relation was tried. These methods are compared with another method below. Other approaches which use FIMS data also are possible, but are not discussed here.

FIMS data generated at SRI International were transferred to CONSOL via ASCII data files, and imported into spreadsheets for additional data processing. The number average molecular weights obtained by this method at CONSOL were consistently lower by a few Da (averaged 5 Da lower, ranged from 2 to 7 Da lower) than the corresponding molecular weights calculated by SRI International. This is an artifact of the data reduction process. It is evidently due to a small loss in mass resolution when the data are converted to unit mass resolution in the software which generates pattern tables and saves the ASCII data file. Any subsequent manipulation of spectral data performed by CONSOL would be subject to this artifact, the effects of which appear to be minor.

In the first of three comparison methods, the THF-insoluble content of a PFL sample was measured and assumed to be unconverted HDPE. This method was applied both to whole PFLs and to PFL resids. The second and third methods are based on FIMS data, and were described above. In Table 14, the results of three methods for estimating the concentration of HDPE in liquefaction process streams are compared. The methods for this limited sample set agree quite well in some cases, and not so well in others. Clearly, there is potential for these methods, but additional work is required. The FIMS approach offers the potential to quantify the amount of unconverted HDPE present in the bottoms (PFC) stream. This would allow a more accurate determination of HDPE conversion than is presently available.

It is anticipated that additional work will be performed to explore and refine methods for plastics quantification. Additional work in solubility characterization will probably be fruitful. Cross-polarization/magic angle spinning (CP/MAS) ^{13}C-NMR is expected to be useful for plastics characterization. Flow

Field-Flow Fractionation (FlFFF) can provide molecular weight distributions of plastics, on either a relative or absolute basis, and thus may be a useful technique. Thermal methods such as thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) offer additional analytical possibilites.

PDMS Analysis Results

Three samples from CMSL-8 Period 22 (the coal/polyethylene period) were analyzed by plasma desorption mass spectrometry (PDMS) to help define the fate of the polyethylene. The analyses were perfomred at Lehigh University under the direction of John Larsen. The samples included the feed high density polyethylene (HDPE), the pressure filter cake (PFC) and the 850 °F$^+$ resid of the pressure filter liquid (PFL) from the coal/HDPE period 22. PDMS sample preparation for analysis requires solubilization of the sample. Lehigh was able to dissolve the resid samples in pyridine at about 50 to 60 °C. However, attempts failed to dissolve HDPE at the same temperature for six days in tetralin, dichlorobenzene, or tetrachloroethane. Consequently, they were able to provide an analysis of the PFC and PFL resid, but not of the feed HDPE. For a mass (m/z) integration range of 78-3000 Da, they reported (Table 15) for the PFL resid, M_N = 705 Da and M_W = 1117 Da, and for the PFC, M_N = 748 Da and M_W = 1224 Da. These molecular weights seemed low, since higher molecular weight components might be expected. In their earlier work with coal liquefaction samples,[3] it was reported that non-polar materials, such as polystyrene, give a low response by PDMS. Larsen confirmed that the method becomes insensitive for polystyrene of molecular weight greater than a few hundred Da, and expected that there is even lower sensitivity for polyethylene.[9] Additional data analysis of the recorded spectra was provided by background correction for the Mylar sample mounting substrate (aluminized Mylar), and by scale expansion of the region from 0-500 Da.

Uncorrected PDMS spectra of the two process samples and a Mylar reference spectrum are shown in Figure 21a-c. Mylar background-corrected, scale-expanded spectra of the two process samples and a scale-expanded Mylar reference spectrum are shown in Figure 21d-e. There is little detail available from the spectra in Figure 21a-b, but the broad hump from about mass 200 Da to mass 3000 Da can be seen, perhaps representing the coal-derived resid.

The prominent Mylar peaks such as the one at ca. 350 Da (Figure 21f) are not seen in the process sample spectra in Figure 21d-e, because of the background correction. One prominent feature in the sample spectra in Figure 21d-e is a peak at ≈148 Da. It can be seen that this peak is rather small in the Mylar reference spectrum, Figure 21f. Other prominent features in the sample spectra in Figure 21d-e are peaks at ≈208, 224, 266, 282 Da, which are evident, but rather small in the Mylar reference spectrum, Figure 21f. These peaks (but not the 148-Da peak) also were seen in the hexane and benzene soluble portion of resids previously analyzed by PDMS.[5] These may be Mylar peaks which are somehow brought into prominence by the background correction procedure.

In light of the sample preparation difficulty, and the apparent lack of correlation between HDPE concentration as found by other methods and PDMS spectral features, PDMS cannot be recommended at this time for characterization/quantification of HDPE in liquefaction streams. It is possible that the technique would be useful for HDPE characterization if a substantial amount of additional development work were done.

Relative to PDMS, it appears that the FIMS analysis benefits from the use of pyrolysis for sample introduction. The pyrolysis of the sample resulted in HDPE ions which were low in molecular weight, and generally distinct from the coal-derived resid ions. Any high molecular weight ions were generally off the mass scale, and were undetected. PDMS uses energetic fission fragments from the decay of ^{252}Cf to volatilize and ionize solid samples.[5] Perhaps this results in larger ion fragments, but does not provide the coal resid and plastic ion distinction observed with FIMS.

Conversion of HDPE During Run CMSL-8

Summary and Introduction

CONSOL and others have found that high-density polyethylene (HDPE) is less reactive than coal and other plastics feedstocks toward liquefaction at conventional liquefaction conditions. Evidence has consisted of the unusual presence of significant concentrations of tetrahydrofuran- (THF-) insoluble material in recycle liquid streams in Runs POC-2 and CMSL-8, unusual solubility and phase behavior in resid-containing and solids-containing streams in Runs POC-2 and CMSL-8, and performance in numerous microreactor and autoclave tests at several

laboratories. Since it appears that adequate conversion of HDPE is an important factor in the development of coal/plastics coprocessing, it is important to know the conversion of the HDPE during Run CMSL-8 and other coal/plastics coprocessing runs. Both single-pass and overall conversions of HDPE during Run CMSL-8 were estimated. It was assumed that the HTI unit was operating at steady-state, that the amount of unconverted HDPE in the pressure-filter liquids (PFLs) was measurable as the amount of tetrahydrofuran- (THF-) insoluble material in the PFLs (i.e., that the PFL THF-insolubles are unconverted HDPE), and that there was no unconverted HDPE in the pressure filter cake (PFC). This was necessary because no method was avilable to determine the concentration of HDPE in the PFC product. During Run CMSL-8, PFL was both the recycle liquid and a liquid product. Overall conversion is defined as fresh HDPE fed which is not present as unconverted HDPE in the net products; in overall HDPE conversion, recycled HDPE is considered an internal stream and does not need to be explicitly accounted for. The single-pass conversion of HDPE is a measure of the disappearance of both the recycled and fresh HDPE fed (recycled HDPE is explicitly accounted for).

The conversion calculations require material balance data for the HTI run periods, and a measure of the amount of HDPE in the pressure-filter liquid and PFC. The unconverted HDPE concentrations in the PFL were estimated based on the THF solubility of the PFL, i.e., THF insolubles in the PFL samples were considered to be unconverted HDPE. Analysis of the PFL sample by Fourier-transform infrared (FTIR) spectroscopy and field-ionization mass-spectrometry (FIMS) supports this assumption. No method was available to determine the HDPE concentration in the pressure-filter cake (PFC) product, and consequently its contribution was ignored. Thus, these results represent an upper limit for conversion.

The estimated overall conversion of HDPE ranged from 40-80 % during the run, lower than the 90-95 % coal conversion and 80-85 % resid conversion typically observed for coal liquefaction. The estimated single-pass conversion of HDPE averaged around 25 %. Both overall and single-pass conversions were lowest during period 16, after an increase in both space velocity and second-stage reactor temperature. Measures taken by HTI to improve performance after period 16, such as reducing the space velocity and doubling the dispersed Mo

catalyst concentration, restored the conversions observed in period 11. Because the conversion was increased by lowering the space velocity in period 18, it appears that space velocity was more important than reactor temperature in determining HDPE conversion in the 830-850 °F range.

Discussion

One way to quantify the reactivity of HDPE when it is coprocessed with coal is to determine the conversion of HDPE in the system and compare it with conversion of coal or coal resid. In the ensuing discussion we assumed that the plant operations were at steady state. The conversion calculations require HTI material balance data for the periods evaluated, and a measure of the amount of HDPE in each of the pressure-filter liquid and pressure filter cake samples from those periods. The wt % unconverted HDPE in each PFL sample was estimated based on the THF solubility of the PFL, and the amount in the PFC was assumed to be zero as described later.

Conversion in either case (overall and single-pass) is defined as

Conversion = [(IN - OUT)/IN] x 100

where IN and OUT are the quantities of HDPE in and out of the process on a mass (or mass flow) basis. However, the calculations are performed differently for overall conversion than for single-pass conversion. For overall conversion, the amount of fresh HDPE fed to the process is the IN quantity, and the total unconverted HDPE found in all the net product streams is the OUT quantity. These values were determined from the HDPE fed as a wt % of dry feed, and from the net adjusted yield of PFL on a wt % dry feed basis (Table 16). To complete the calculation, it is necessary to know the wt % unconverted HDPE in the PFL, which was estimated using CONSOL analyses, as described below.

For single-pass conversion, the total of fresh and recycle HDPE is the IN quantity, and the total unconverted HDPE in collected products (including recycle) is the OUT quantity. For this calculation, a number of individual flows contributing to the PFL recycle were summed and added to the fresh feed contribution. These included small flows of PFL for pump seals and purges. When continuous atmospheric still (CAS) bottoms was recycled in one period, the

pressure-filter cake contribution from the CAS bottoms was subtracted, and only the PFL portion was considered. The PFL flow out was obtained from HTI material balances, as were the other flows.[1]

Only HDPE in the PFL was considered; that is, any HDPE in the PFC product was ignored. This was necessary, because we currently have no method to quantify HDPE in the PFC samples. However, the total organic and ash concentrations in the PFC samples from coal/plastics periods of operation are not substantially different from the corresponding PFC sample from the coal-only period. Thus, the data suggest that these PFC samples cannot contain a substantial amount of plastic-derived material. To the extent that HDPE in the PFC samples is unaccounted, this contribution to the product HDPE is ignored, and the overall and single-pass conversions given here are upper limits. If a method is developed for determining the amount of HDPE in the PFC samples, we will use such data to correct the calculated overall and single-pass conversions for the HDPE in the PFC stream.

One estimate of wt % HDPE in PFL is the wt % THF-insoluble portion of the whole PFL. The presence of THF insolubles in the PFL is a unique feature of coal/plastics processing. PFLs from coal-only operations typically contain little or no THF-insoluble material. It was confirmed using Fourier-transform infrared (FTIR) spectroscopy and field-ionization mass spectrometry (FIMS) that this THF-insoluble material is predominantly HDPE-derived. Using THF insolubility to estimate unconverted HDPE in the PFL incurs some positive and negative errors. Non-HDPE components in the THF-insoluble material would result in a high estimate for HDPE. On the other hand, some portion of the incompletely converted HDPE may be soluble in THF, which would give a low estimate for unconverted HDPE by this approach. We determined the amount of THF-insoluble material in the whole PFL, and in the PFL 850 °F$^+$ resid after distillation (Table 16). The THF-insoluble material content on a wt % PFL basis determined from the two sample sets agreed within a few percent absolute. Thus, this approach to estimating HDPE content in the PFL provides analytically consistent results.

The overall and single-pass conversions are given in Table 16, based on the estimates for HDPE in the PFL as described above. The conversions obtained using the

THF insoluble component in the whole PFL agrees well with those obtained using the THF insoluble component in the PFL resid. For the sake of discussion, we will concentrate on the first set shown in the table (based on THF insolubles in the whole PFL): 44.6 to 80.7% overall conversion, and 9.1 to 49.5% single-pass conversion. The overall conversion was 71.6 to 80.7% in periods 11, 20, and 22, but only 44.6% in period 16. In period 12, HTI increased the space velocity from 30 to 40 lb dry feed/h/ft^3 reactor and increased the second-stage reactor temperature from 830 °F to 850 °F. At this point in the run, declining activity of the supported catalyst could also affect conversion. Evidently, these factors contributed to substantially decreased overall conversion of HDPE in period 16. Between periods 16 and 20, with a higher proportion of plastics in the feed, HTI reduced the space velocity to 30 lb dry feed/h/ft^3 reactor in period 18 and doubled the concentration of dispersed Mo catalyst in period 19, in order to improve process performance. These adjustments improved the HDPE conversion nearly back to the 80% observed in period 11. These results seem to indicate that lower space velocity was more important than higher second-stage temperature in producing relatively high conversion of HDPE. Like the overall conversions, the single-pass conversions were about the same in periods 11 and 20 (23.2 and 26.2%, respectively), and much lower in period 16 (9.1%). However, the single-pass HDPE conversion in period 22 was much higher at 49.5%. Measures that HTI took to maintain operability in that period of the run when HDPE and coal were fed seemed to provide the high single-pass conversion and high overall conversion of HDPE. However, HTI found the plant increasingly difficult to operate, having difficulty with filtration operation, and taking increasing amounts of PFL liquid out as product. The results presented here indicate that the overall conversion of HDPE was lower than the 90-95% coal conversions and 80-85% resid conversions typical for coal liquefaction. The single-pass HDPE conversions averaged around 25%.

UNIVERSITY OF DELAWARE SAMPLE ANALYSIS

The solids portion of twenty-nine reaction products from experiments performed in Delaware's STBR were received for C, H, N, S (total), O (by diff.), and ash analysis and ash elemental analysis. These samples were produced from the 850 °F$^+$ resid of Wilsonville Run 258 V131 B (recycle stream) using either molybdenum naphthenate and dimethyldisulfide or Ni/Mo on alumina catalyst. STBR conditions were 400 °C to 422 °C and 1 to 60 min. From the Ni and Mo content in the ash and the ash content of the initial resid, Delaware will determine the amount of supported catalyst in the sample. The results of the analyses are provided in Table 17.

Section 4
EXPERIMENTAL

HTI RUN CMSL-8

All samples analyzed for proton distribution by NMR spectroscopy were dissolved in 99.96% deuterated pyridine (whole or resid samples) or in $CDCl_3$ (distillate samples) and integrated electronically. The solids-containing whole samples were sonicated with deuterated pyridine and filtered for analysis by ^{1}H-NMR.

Response factors used for flame ionization detection of solubility fractions from coal-only period 6 were those previously used for samples produced from Burning Star 2, Illinois 6 coal. A different set of response factors is normally used for each feed coal used to produce an oil sample. New response factors for coal/plastics co-liquefaction (periods 11 through 23) were obtained based on analytical scale (fractions were detected by a flame ionization detector) and preparative scale (fractions were collected and weighed) runs with four selected samples. The four samples selected for response factor determination were one PFL resid THF extract and one PFC THF extract from each of the CMSL-8 run periods 11 (coal/mixed plastics) and 22 or 23 (coal/HDPE).

GC-MS analyses were done with a DB-5 column, 30 m x 0.25 mm, 0.25 μm film thickness. The carrier gas was He at 20 psig. The injection port was held at 300 °C and injections were made in the splitless mode. The mass spectrometer was scanned from 33 to 300 amu. Peak identifications were based on searches of the Wiley/NBS mass spectral library and retention times. For SOH and ASOH samples, injected neat, the GC conditions were: 5 min at 10 °C, 2 °C/min to 100 °C, 4 °C/min to 320 °C, up to 20 min at 320 °C. For CAS bottoms distillate samples, injected as one-percent solutions in tetrahydrofuran, the GC conditions were: 5 min at 35 °C; 35 °C/min to 100 °C, 4 °C/min to 320 °C, up to 20 min at 320 °C.

Other details of the sample work-up and analytical procedures have been presented elsewhere.[10,11]

Section 5
REFERENCES

1. Pradhan, V. R. "Run CMSL-8, Evaluation of Coal-Plastics Co-Liquefaction in CTSL Mode", Draft HTI Report (DOE Contract No. DE-AC22-93PC92147), January, 1995.

2. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "A Characterization and Evaluation of Coal Liquefaction Process Streams, Quarterly Technical Progress Report October 1 through December 31, 1994", DOE/PC 93054-10, May 1995.

3. Robbins, G. A.; Winschel, R. A.; Burke, F. P. "Characterization of Coal/Waste Coprocessing Samples from HRI Run POC-2", Prepr. Am. Chem. Soc., Div. Fuel Chem., 40 (1) 1995, Anaheim, CA, April 1995, pp. 92-96.

4. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "Coal Liquefaction Characterization and Evaluation, Final Report, Volume I, Base Program Activities", DOE/PC 89883-93, May 1994.

5. Larsen, J. W.; Lapucha, A. R. "Coal Liquefaction Process Streams Characterization and Evaluation, The Application of ^{252}Cf-Plasma Desorption Mass Spectrometry to Analysis of Direct Coal Liquefaction Heavy Products", DOE/PC 89883-58, October 1992.

6. Malhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation, Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization", DOE PC 89883-39, January 1992.

7. Malhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation, FIMS Analysis for Direct Coal Liquefaction Process Streams", DOE/PC 89883-91, March 1994.

8. R. Malhotra, personal communication.

9. J. W. Larsen, personal communication.

10. Burke, F. P.; Winschel, R. A.; Robbins, G. A. "Recycle Slurry Oil Characterization, Final Report, October 1980 through March 1985", DOE/PC 30027-61, March 1985.

11. Winschel, R. A.; Robbins, G. A., Burke, F. P. "Coal Liquefaction Process Solvent Characterization and Evaluation, Technical Progress Report, July 1985 through September 1985", DOE/PC 70018-13, December 1985.

TABLE 1

RUN CONDITIONS AND PROCESS PERFORMANCE SUMMARY FOR HTI RUN CMSL-8 (227-85)

Condition	1	2	3	4	5
Period No.	1-6*	7-11*(b)	12-16*	17-20*	21,22*,23*
Hours of Run (End of Period)	144	264	384	480	528
wt % Plastics in Feed (a)	0	25	25	33	33
Stage 1 Cat. Age, lb Feed/lb Cat	252	457	711	884	966
Stage 1 Feed Space Velocity lb Feed/hr/ft^3 Reactor Vol.	32.2	29.6	39	30.1(c)	29.6
Oils/Solids Ratio	1.5	1.6	1.8	2.1	1.9
Temperature, °F					
Stage 1	810	810	810	810	810
Stage 2	830	830	850	850	850
HTU	715	715	715	715	715
Dispersed Mo Concentration, ppm of Dry Feed	100	100	100	200(c)	200
Total Material Recovery, % (Gross)	102.2	98.4	96.7	101.2	99.6
Estimated Normalized Yields, wt % MAF Feed					
C_1-C_3 in Gases	11.35	9.14	9.02	7.41	5.17
C_4-C_7 in Gases	4.81	3.27	3.41	3.17	3.27
IBP-350 °F	15.86	20.48	19.00	17.63	8.80
350-500 °F	17.99	12.57	8.59	11.16	7.60
500-650 °F	21.14	19.85	12.27	16.88	10.72
650-850 °F	10.18	11.84	15.18	11.54	14.24
850-975 °F	2.29	2.94	5.60	4.22	6.43
975 °F$^+$	4.74	10.53	17.15	19.67	33.83
Unconverted Feed	3.90	4.07	4.50	4.40	4.22
Water	9.04	7.34	6.90	5.92	4.85
COx	0.67	0.80	0.86	0.57	0.16
NH_3	1.50	1.08	1.04	0.82	0.27
H_2S	3.98	2.98	2.84	2.52	2.24
Hydrogen Consumption	7.46	6.91	6.35	5.71	1.80
Process Performance					
Feed Conversion, wt % MAF Feed	96.10	95.90	95.50	95.60	95.80
975 °F$^+$ Conversion, wt % MAF Feed	91.40	85.40	78.40	75.90	62.00
C_4-975 °F Distillates, wt % MAF Feed	72.30	71.00	64.00	64.40	51.00
Hydrogen Efficiency, lb Dist/lb H_2	9.69	10.27	10.08	11.28	28.33

Feeds:
Illinois No. 6 Crown II Mine coal, HDPE, Polystyrene, and PET
Back Pressure: 2500 psig

Catalysts:
K-1: Shell 317 Supported + Dispersed Sulfated Fe/Mo Oxide (100 ppm Mo)
K-2: Only Dispersed Sulfated Fe/Mo Oxide Introduced in Feed to K-1
Hydrotreater: HRI-6135 (Criterion C-411 Trilobe)

(a) Conditions 2-4 used a 50/35/15 w/wt % ratio of HDPE/PS/PET; Condition 5 used HDPE alone w/coal.

(b) Although not specifically listed here, in period 9 the in-line hydrotreater (HTU) was by-passed; otherwise conditions were the same as in period 11.

(c) The total space velocity was reduced from 40 to 30 beginning in Period 18 as a result of operating difficulties at higher space velocities; the dispersed catalyst addition rate also was increased from 100 ppm Mo to 200 ppm Mo beginning in Period 19 to improve process performance.

* Indicates sample period. Samples were the best available; they were taken at the end of material balance periods that were usually three days each in duration.

TABLE 2

ANALYSIS OF COAL AND PLASTIC[a] FEEDSTOCKS FOR RUN CMSL-8

HRI No.	L-811	6235	6236	6237
Material	Illinois 6	HDPE	Polystyrene	PET
Moisture Content	4.00			
Proximate Analysis, wt % Dry Basis				
Volatile Matter	41.48			
Fixed Carbon	48.08			
Ash	10.44			
Ultimate Analysis, wt % MAF Basis				
Carbon	67.85	85.27	90.81	61.9
Hydrogen	4.55	14.61	7.71	4.13
Sulfur	3.99	0.037	0.01	0.01
Nitrogen	1.33	0.01	0.06	0.03
Oxygen, by diff.	11.36	0.073	1.41	33.9
H/C Atomic Ratio	0.81	2.06	1.02	0.80

(a) All three plastics initially were completely insoluble in either quinoline or cyclohexane.

TABLE 3

ANALYSIS OF START-UP/MAKE-UP OIL FOR RUN CMSL-8

HRI No.	L-814
API Gravity	0.4
Elemental Analysis, wt %	
Carbon	88.96
Hydrogen	8.25
Sulfur	2.22
Nitrogen	0.19
ASTM D-1160 Distillation, vol % at °F	
IBP	588
5	664
10	706
20	742
30	769
40	798
50	819
60	840
70	873
80	944
84	975
wt %	
IBP-650 °F	5.00
650-850 °F	53.99
850-975 °F	22.18
975 °F$^+$	18.36
Loss	0.47
% Aromatic Carbon	80.03
% Cyclic Hydrogen	44.36

TABLE 4

CONSOL ANALYSES OF SAMPLES
FROM HTI COAL/PLASTICS CO-LIQUEFACTION RUN CMSL-8

Sample Description; Name (Abbrev.); Sample Point	Periods	Technique & Information Sought (Refer to Key)
Atmospheric Overheads; CAS Overheads or Atmospheric Still Overheads (ASOH); SP-3	9 (HTU Bypass)	A,B,C
Product Distillate; Separator Overheads (SOH); SP-4	6,9,11,16,20,23	A,B,C
Filtration Feed; CAS Bottoms; SP-5	6,11,16,20,23	A,F,G; THFS - B; Dist. - A,B,C,E; Resid - G; Resid THFS - A,B,H
Recycle Oil; Pressure Filter Liquid (PFL); SP-6	6,11,16,20,22	A,E,F,G; THFS - B; THFI - D; Dist. - A,B,E; Resid - G; Resid THFS - A,B,H
Solid Residue; Pressure Filter Cake (PFC); SP-7	6,11,16,20,22	G; THFS -A,B,H

Note: THFS = THF Soluble Fraction; THFI = THF Insoluble Fraction

KEY TO TECHNIQUES AND INFORMATION SOUGHT:

A = ^{1}H-NMR for hydrogen distribution (7 classes), aromaticity (degree of hydrogenation), paraffinicity, hydrogen donors
B = FTIR in THF solution for phenolic -OH content
C = GC-MS for composition, carbon numbers of paraffins
D = special analyses
E = microautoclave test with standard coal for donor solvent quality
F = 850°F distillation for distillate content
G = THF extraction and ash for resid, ash and IOM content, for coal and resid conversion
H = solvent fractionation (oils, asphaltenes, preasphaltenes) for resid composition.

TABLE 5

COMPONENT DISTRIBUTION OF WHOLE SAMPLES
HTI RUN 227-85 CMSL-8

Sample Type	Period	HTI No. LO-	Lab No. 1621-33-	wt % of Sample			Ash	Distillation Balance	THF Extraction, Whole Sample*, %		
				850 °F⁻ Dist.	850 °F⁺ Resid	IOM			Resid	IOM	Ash
PFL	6	6534	272	55.0	43.9	0.2	<0.1	99.10	99.98	0.02	<0.01
	11	6535	273	39.7	39.0	20.3	<0.1	99.00	79.98	20.02	<0.01
	16	6536	274	35.0	25.5	37.4	<0.1	97.90	69.56	30.44	<0.01
	20	6537	275	27.6	54.8	16.5	0.1	99.00	85.50	14.50	<0.01
	22	6538	276	17.5	65.3	15.8	<0.1	98.60	81.43	18.57	<0.01
PFC	6	6539	277	-	-	-	-	0.00	41.20	14.20	44.60
	11	6540	278	-	-	-	-	0.00	30.70	25.60	44.00
	16	6541	279	-	-	-	-	0.00	28.10	26.60	45.30
	20	6542	280	-	-	-	-	0.00	31.10	26.90	42.00
	23	6543	281	-	-	-	-	0.00	24.90	27.50	47.60
CAS Btms	6	6522	260	53.4	38.5	2.1	5.3	99.30	94.70	1.40	3.90
	11	6523	261	44.8	32.9	21.7	0.4	99.80	69.90	30.10	<0.01
	16	6524	262	38.2	42.5	16.1	2.3	99.10	85.60	11.10	3.30
	20	6525	263	32.3	46.4	20.2	0.7	99.60	62.70	36.80	0.50
	23	6526	264	23.0	55.5	21.3	<0.1	99.80	35.00	65.00	<0.01

*THF Extraction of whole samples: PFL, PFC and CAS Btms.

TABLE 6

SOLUBILITY FRACTIONATION OF SAMPLES
HTI RUN 227-85 CMSL-8

Sample Type	Period	Lab No. 1621-33-	wt % of THF Solubles			Lab No. 1621-33-	wt% 850 °F$^+$ Resid THF Solubles		
			Oils	Asphaltenes	Preasphaltenes		Oils	Asphaltenes	Preasphaltenes
PFL	6(a)	272	74.4	18.2	7.4	282	68.8	22.1	9.0
	11(b)	273	75.9	15.4	8.7	283	59.3	23.8	16.8
	16(b)	274	77.2	12.1	10.7	284	76.1	19.3	4.6
	20(b)	275	51.5	22.0	26.6	285	46.9	27.3	25.8
	22(b)	276	49.7	25.1	25.2	286	48.9	29.5	21.6
PFC	6(a)	277	69.2	21.2	9.6	-	-	-	-
	11(b)	278	65.1	15.7	19.2	-	-	-	-
	16(b)	279	60.8	16.9	22.3	-	-	-	-
	20(b)	280	52.3	21.7	26.0	-	-	-	-
	23(b)	281	47.8	21.3	30.9	-	-	-	-
CAS Btms	6(a)	260	77.9	14.7	7.4	402	69.0	21.7	9.4
	11(b)	261	84.3	8.4	7.3	403	60.8	23.4	15.8
	16(b)	262	61.1	19.4	19.5	404	50.2	23.5	26.3
	20(b)	263	77.9	14.9	7.2	405	57.6	20.2	22.3
	23(b)	264	77.2	13.0	9.8	406	65.3	19.3	15.4

(a) Determined Using Burning Star, Illinois 6 Response Factors: O = 0.4437, A = 0.1518, P = 0.4046
(b) Determined Using Run CMSL-8 Coal/Plastic Response Factors: O = 0.3348, A = 0.1340, P = 0.5311

TABLE 7

PROTON DISTRIBUTION OF WHOLE SAMPLES
HTI RUN 227-85 CMSL-8

Sample Type	Period	HTI No. LO-	Lab No. 1621-33-	Proton Distribution, %						
				Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
SOH	6	6527	265	3.3	0.3	4.1	4.5	26.3	33.5	28.1
	9	6528	266	6.6	11.1	7.8	9.3	16.7	30.4	18.2
	11	6529	267	3.1	3.3	3.5	4.3	24.4	35.7	25.8
	16	6530	268	3.3	6.7	5.2	6.2	18.7	37.2	22.7
	20	6531	269	2.8	5.2	4.3	5.4	17.7	38.9	25.7
	23	6532	270	0.7	2.1	3.5	2.4	24.6	38.1	28.5
ASOH	9	6533	271	5.8	11.1	10.0	10.9	18.7	26.4	17.1
PFL	6	6534	272	19.8	9.8	15.8	11.2	13.9	17.8	11.7
	11	6535	273	17.3	7.5	13.3	8.9	11.7	29.0	12.3
	16	6536	274	15.2	6.0	11.4	8.4	10.4	35.6	13.1
	20	6537	275	14.3	7.0	11.7	8.4	11.5	33.2	13.9
	22	6538	276	25.6	8.6	17.0	10.7	11.9	16.1	10.0
PFC	6	6539	277	25.2	4.6	17.7	10.6	14.5	17.0	10.5
	11	6540	278	27.1	4.7	17.1	10.0	12.4	18.6	10.2
	16	6541	279	27.5	5.9	15.5	10.2	10.7	20.4	9.8
	20	6542	280	27.2	7.0	14.9	10.1	10.6	20.1	10.1
	23	6543	281	30.6	8.9	17.6	11.2	10.8	13.0	7.8
CAS Btms	6	6522	260	22.2	6.9	16.8	10.8	14.0	17.1	12.2
	11	6523	261	20.1	5.0	13.6	9.5	13.1	25.2	13.5
	16	6524	262	24.6	7.5	13.6	10.6	10.6	21.2	11.9
	20	6525	263	20.6	4.5	13.5	9.7	12.1	27.0	12.5
	23	6526	264	19.0	4.5	14.9	9.9	13.1	26.0	12.7

TABLE 8

PROTON DISTRIBUTION OF DISTILLATES
HTI RUN 227-85 CMSL-8

Sample Type	Period	HTI No. LO-	Lab No. 1621-33-	Proton Distribution, %						
				Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
850 °F⁻ Distillates										
PFL	6	6534	292	17.6	7.2	15.7	11.0	15.6	20.5	12.5
	11	6535	294	16.3	5.7	12.9	9.3	12.9	30.0	12.9
	16	6536	296	13.9	5.9	9.3	8.4	10.8	36.6	15.0
	20	6537	410	17.1	8.4	12.3	10.8	11.3	27.4	12.6
	22	6538	412	17.8	8.9	13.8	11.5	12.6	23.4	12.0
CAS Btms	6	6522	336	16.8	7.9	14.8	11.2	15.2	20.9	13.1
	11	6523	337	14.6	6.9	11.7	9.4	12.7	30.7	13.9
	16	6524	339	15.3	8.0	10.3	10.3	10.3	31.3	14.6
	20	6525	342	13.5	8.1	9.8	10.0	11.1	32.7	14.8
	23	6526	344	13.8	6.9	12.2	9.5	12.8	31.2	13.6

TABLE 9

PROTON DISTRIBUTION OF RESIDS
HTI RUN 227-85 CMSL-8

Sample Type	Period	HTI No. LO-	Lab No. 1621-33-	Proton Distribution, %						
				Cond Arom	Uncond Arom	Cyclic Alpha	Alkyl Alpha	Cyclic Beta	Alkyl Beta	Gamma
850 °F+ Resids										
PFL	6	6534	293	32.4	6.5	19.9	10.2	12.2	11.5	7.4
	11	6535	295	26.7	11.8	17.5	10.9	10.5	14.5	8.0
	16	6536	297	30.6	4.6	16.6	9.4	11.0	19.2	8.6
	20	6537	411	34.1	8.5	18.5	10.7	10.8	11.2	6.2
	22	6538	413	31.0	8.7	19.2	10.7	11.8	11.8	6.9
CAS Btms	6	6522	409	33.6	7.3	18.7	10.1	12.4	10.9	7.0
	11	6523	338	34.1	6.0	18.9	9.7	10.9	13.1	7.2
	16	6524	340	34.3	6.8	16.6	10.7	10.5	13.4	7.8
	20	6525	343	31.3	8.1	17.2	9.9	10.6	15.4	7.5
	23	6526	345	29.1	4.3	15.9	9.0	13.4	19.5	8.8

TABLE 10

PHENOL CONCENTRATION BY FTIR
HTI RUN 227-85 CMSL-8

Sample Type	Period	HTI LO-	Lab No. 1621-33-	Phenolic -OH Concentrations, meq/g										
				Whole Conc.	Whole Pk, cm^{-1}	Lab No. 1621-33-	Dist. Conc.	Dist. Pk, cm^{-1}	Lab No. 1621-33-	Resid Conc.	Resid Pk, cm^{-1}	Lab No. 1621-33-	THF Sol Conc.	THF Sol Pk, cm^{-1}
PFL	6	6534	272	0.64	3299	292	0.38	3306	293	0.83	3293	282	0.65	3298
	11	6535	273	0.41	3301	294	0.47	3306	295	0.84	3294	283	0.64	3300
	16	6536	274	0.32	3302	296	0.43	3307	297	0.68	3298	284	0.52	3301
	20	6537	275	NA	NA	410	0.75	3305	411	0.98	3291	285	0.96	3296
	22	6538	276	NA	NA	412	0.84	3307	413	1.03	3293	286	1.13	3295
SOH	6	6527	265	ND	3357									
	9	6528	266	0.51	3313									
	11	6529	267	ND	3356									
	16	6530	268	ND	3358									
	20	6531	269	ND	3356									
	23	6532	270	ND	3355									
ASOH	9	6533	271	0.79	3313									
CAS Btms	6	6522	260	0.62	3299									
	11	6523	261	0.44	3303									
	16	6524	262	0.91	3299									
	20	6525	263	0.62	3301									
	23	6526	264	0.67	3302									
PFC	6	6539	277	0.61	3297									
	11	6540	278	0.76	3297									
	16	6541	279	0.76	3295									
	20	6542	280	0.87	3297									
	23	6543	281	1.06	3294									

TABLE 11

MICROAUTOCLAVE CONVERSIONS
HTI RUN 227-85 CMSL-8

Sample Type	Period	HTI No. LO-	Lab No. 1621-33-	Coal Conversion, wt % MAF
Whole Sample				
PFL	6	6534	292	71.5
	11	6535	294	18.2
	16	6536	296	31.5
	20	6537	410	<1.0
	22	6538	412	36.8
CAS Bottoms	6	6522		
	11	6523		
	16	6524		
	20	6525		
	23	6526		
Distillates				
PFL	6	6534	272	77.6
	11	6535	273	67.6
	16	6536	274	58.5
	20	6537	275	68.6
	22	6538	276	77.5
CAS Bottoms	6	6522	336	77.2
	11	6523	337	61.6
	16	6524		
	20	6525		
	23	6526		

TABLE 12

QUANTITATION OF POLYSTYRENE LIQUEFACTION PRODUCTS IN SOH PRODUCT OILS FROM HTI RUN CMSL-8

Period	Analysis by GC-MS, Area % of SOH Total Ion Chromatogram			Analysis by ^{1}H-NMR	wt % PS in Dry Feed	SOH Yield, wt % of Dry Feed	EB+IPB by GC-MS, as wt % of PS Fed	EB by ^{1}H-NMR, as wt % of PS Fed
	Ethylbenzene, Ret. Time ca. 16.7 min.	Cumene (Isopropylbenzene), Ret. Time ca. 21.8 min.	Total, Area % (assumed to equal wt % of SOH)	As Ethylbenzene, wt % from Integration of Peak at 7.1 ppm				
6 (Coal)	0.55	-	0.55	-	0	50.06	- (b)	-
11 (Coal/Mixed Plastics)	6.53	1.91	8.4	8.8	8.75	47.65	45.7	47.9
16 (Coal/Mixed Plastics)	8.32	3.38	11.7	15.1	8.75	33.52	44.8	57.8
20 (Coal/Mixed Plastics)	6.94	2.01	9.0	12.1	11.55	43.28	33.7	45.3
23 (Coal/HDPE)	1.38	0.29	1.7	3.4	0	25.29	(c)	(d)
9 (Coal/Mixed Plastics - HTU Off-line)	13.52	4.03	17.6	15.4 (a)	8.75	35.02	70.4	61.6

(a) Assumed 11 wt % H in SOH for NMR estimate, other periods used wt % H reported by HTI.[1]
(b) Represents 0.3 wt % of dry coal fed; equivalent to 3.1 wt % of PS fed in period 11.
(c) Represents 0.6 wt % of dry coal fed; equivalent to 3.7 wt % of PS fed in period 20.
(d) Represents 1.2 wt % of dry coal fed; equivalent to 7.4 wt % of PS fed in period 20.

TABLE 13

ESTIMATION OF HDPE CONCENTRATION WITH FIMS DATA

Sample	FIMS M_N, Da	FIMS M_W, Da	Estimate of wt % HDPE, Based on M_N(a)	M_W/M_N	Estimate of wt % HDPE, Based on M_W/M_N(b)
HDPE	154	558	100	3.62	100
PFL 22 THFI(c)	184	662	93	3.60	99
PFC 22	304	591	66	1.94	31
PFL 22	329	493	61(d)	1.50	13(d)
PFL 11 Resid Top Layer	404	627	44	1.55	15
PFL 22 THFS (c)	426	534	39(d)	1.25	3(d)
PFL 11 Resid Bottom Layer	466	580	30	1.24	3
THF-Soluble Coal Resids[5,6]	600	710	-	1.18	-

Note: FIMS analyses were performed by R. Malhotra, at SRI International.

(a) It was assumed that wt % HDPE is linearly related to M_N, and that M_N = 154 Da for 100% HDPE, and M_N = 600 Da for 100% coal resid.[5,6]

(c) THFI = THF insolubles; THFS = THF solubles.

(b) It was assumed that wt % HDPE is linearly related to M_W/M_N, and that M_W/M_N = 3.62 for 100% HDPE, and M_W/M_N = 1.18 for 100% coal resid.[5,6]

(d) Uncorrected for distillate with M_N <<600 Da.

TABLE 14

COMPARISON OF METHODS TO ESTIMATE HDPE CONCENTRATION

Sample	Estimate of HDPE as THF Insolubles, wt % of Sample		Estimate of wt % HDPE, Based on M_N	Estimate of wt % HDPE, Based on M_W/M_N
	From Whole Sample	From Resid		
PFL 22 THFI	100	-	93	99
PFL 22 THFS	0.0	-	(b)	3
PFL 22	18.6	15.8	(b)	13
PFL 11 Resid Top Layer	-	-	44	15
PFL 11 Resid Bottom Layer	-	-	30	3
PFL 11	20.0	20.3	23(a)	7(a)

(a) Calculated from wt % HDPE in each resid layer, the wt % of each layer in the resid (66.7 wt % top layer, 33.3 wt % bottom layer), and 59.3 wt % resid in the PFL.

(b) Correction for distillate with M_N <<600 Da would be required.

TABLE 15

PDMS AND FIMS MOLECULAR WEIGHT DATA

SAMPLE	PDMS			FIMS		
	M_N, Da	M_W, Da	M_W/M_N	M_N, Da	M_W, Da	M_W/M_N
HDPE	-	-	-	154	538	3.6
PFC 22	748	1224	1.6	304	591	1.9
PFL 22 Whole	-	-	-	329	493	1.5
PFL 22 Resid	705	1117	1.6	-	-	-
PFL 22 THFI	-	-	-	184	662	3.6
PFL 11 Plastic Layer	-	-	-	466	580	1.2
PFL 11 Coal Layer	-	-	-	404	627	1.6
Previous Resids[5]	600	1350	2.3	600	700	1.2

TABLE 16

ESTIMATED OVERALL AND SINGLE-PASS CONVERSIONS OF HDPE DURING HTI RUN CMSL-8

Period	wt % HDPE in PFL (a)	HDPE In, wt % Dry Feed (b,c)	PFL Product, wt % Dry Feed (b)	HDPE Product, wt % Dry Feed (c)	Estimated Overall Conversion, % (c)	Fresh HDPE Feed, g/h (b,c)	Recycle HDPE In, g/h (b,c)	Total HDPE In, g/h (b,c)	HDPE Out, g/h (b,c)	Estimated Single-Pass Conversion, % (c)
Using THF insolubles in whole PFL as estimate for HDPE in PFL:										
11	20.0	12.5	12.02	2.4	80.7	118.5	306.0	424.5	326.2	23.2
16	30.4	12.5	22.74	6.9	44.6	156.2	700.7	856.9	779.3	9.1
20	14.5	16.5	32.30	4.7	71.6	159.3	295.1	454.4	335.5	26.2
22	18.6	33.0	46.33	8.6	73.9	312.9	357.6	670.6	338.5	49.5
Using THF insolubles in PFL resid as estimate for HDPE in PFL:										
11	20.3	12.5	12.02	2.4	80.5	118.5	310.2	428.8	330.7	22.9
16	37.4	12.5	22.74	8.5	32.0	156.2	860.9	1017.1	957.4	5.9
20	16.5	16.5	32.30	5.3	67.7	159.3	335.8	495.1	381.8	22.9
22	15.8	33.0	46.33	7.3	77.8	312.9	304.3	617.2	288.0	53.3

(a) Assuming that THF insolubles in PFL are unconverted HDPE.
(b) From HTI daily material balance data, Reference 1.
(c) Calculated from HTI and CONSOL data.

TABLE 17

ANALYSIS OF SOLID PORTION OF STBR REACTION PRODUCTS (UNIVERSITY OF DELAWARE SAMPLE SET)

CONSOL Sample No.	346	347	348	349	350	351	352	353	354	355
Delaware Sample No.	CO01 (S)	CO02(S)	CO04(S)	CO06(S)	CO07(S)	CO08(S)	CO09(S)	CO14(S)	CO15(S)	CO17(S)
Ultimate, wt%										
C	58.71	59.32	53.27	51.22	53.08	55.55	46.94	52.82	49.43	53.15
H	2.76	2.60	2.33	2.24	2.24	2.43	2.16	2.46	2.29	2.59
N	1.08	1.11	1.01	0.99	1.04	0.91	0.85	0.84	0.86	0.94
S	3.21	3.20	3.57	3.92	3.82	4.49	5.77	3.79	3.82	3.58
Ash	39.27	34.48	42.71	44.97	43.50	40.13	49.50	43.78	46.68	42.20
O (by difference)	-5.03	-0.71	-2.89	-3.34	-3.68	-3.51	-5.34	-3.69	-3.23	-2.46
Ash Elementals, wt% of ash										
MoO_3	0.09	0.05	0.02	0.01	0.02	7.11	7.39	3.27	7.38	4.51
NiO	0.06	0.00	0.03	0.02	0.04	0.03	0.03	0.03	0.01	0.01
SiO_2	24.70	26.63	24.17	24.24	24.29	21.93	21.55	24.48	21.88	23.00
Al_2O_3	13.18	13.45	13.07	12.82	12.66	11.65	11.48	13.09	11.82	12.31
TiO_2	0.95	0.97	0.95	0.93	0.92	0.84	0.85	0.95	0.87	0.91
Fe_2O_3	21.99	21.95	21.04	20.82	20.82	19.45	18.91	21.67	19.86	19.81
CaO	14.25	14.47	14.28	14.26	13.92	12.42	12.95	12.55	12.83	13.37
MgO	3.41	3.42	3.40	3.37	3.32	2.73	2.98	2.75	3.03	3.16
Na_2O	1.84	1.84	1.88	1.79	1.83	1.54	1.59	1.63	1.65	1.74
K_2O	0.48	0.48	0.42	0.42	0.41	0.38	0.38	0.43	0.41	0.41
P_2O_5	0.60	0.59	0.59	0.59	0.57	0.47	0.46	0.57	0.47	0.51
SO_3	16.40	15.00	19.34	19.62	19.99	18.16	19.88	17.90	16.47	18.25
Unaccounted	2.05	1.14	0.81	1.11	1.21	3.29	1.55	0.68	3.32	2.01

TABLE 17 (Continued)

ANALYSIS OF SOLID PORTION OF STBR REACTION PRODUCTS (UNIVERSITY OF DELAWARE SAMPLE SET)

CONSOL Sample No.	356	357	358	359	360	361	362	363	364	365
Delaware Sample No.	CO018(S)	CO019(S)	CO20(S)	CO21(S)	CO22(S)	CO24(S)	CO25(S)	CO26(S)	CO27(S)	CO28(S)
Ultimate, wt%										
C	49.73	51.64	49.43	51.96	47.53	42.68	20.22	15.67	18.82	16.46
H	2.30	2.41	2.18	2.18	1.94	1.81	1.15	1.01	1.05	0.89
N	0.85	0.84	0.81	0.89	0.80	0.67	0.57	0.55	0.48	0.48
S	5.44	5.19	5.44	5.13	5.42	6.19	6.28	6.21	5.89	6.08
Ash	45.93	44.47	47.24	45.12	49.94	54.34	69.82	74.77	73.37	76.31
O (by difference)	-4.35	-4.55	-5.22	-5.28	-5.75	-5.84	1.67	1.55	0.14	-0.38
Ash Elementals, wt% of ash										
MoO_3	6.77	6.96	7.07	6.54	6.51	7.00	14.79	16.03	15.51	15.74
NiO	0.01	0.01	0.06	0.10	0.05	0.04	2.80	2.89	2.81	2.80
SiO_2	21.98	21.74	21.51	20.95	21.02	21.56	2.64	1.63	2.29	2.22
Al_2O_3	11.86	11.61	11.36	11.26	11.60	11.86	60.90	63.73	61.58	62.40
TiO_2	0.86	0.87	0.85	0.83	0.84	0.86	0.17	0.14	0.17	0.15
Fe_2O_3	19.73	19.13	20.09	21.08	19.05	19.32	2.83	1.62	2.21	2.04
CaO	12.22	12.32	12.52	12.90	12.41	12.82	1.62	1.07	1.46	1.35
MgO	2.84	2.97	2.96	2.89	3.07	3.14	0.37	0.24	0.34	0.30
Na_2O	1.67	1.68	1.64	1.61	1.63	1.67	0.25	0.16	0.24	0.21
K_2O	0.39	0.39	0.38	0.40	0.40	0.40	0.06	0.05	0.05	0.04
P_2O_5	0.46	0.46	0.44	0.43	0.48	0.48	6.94	7.26	7.05	7.15
SO_3	19.46	18.83	19.86	19.92	19.70	17.89	1.65	1.11	1.63	1.57
Unaccounted	1.75	3.03	1.26	1.09	3.24	2.96	4.98	4.07	4.66	4.03

TABLE 17 (Continued)

ANALYSIS OF SOLID PORTION OF STBR REACTION PRODUCTS (UNIVERSITY OF DELAWARE SAMPLE SET)

CONSOL Sample No.	366	367	368	369	370	371	372	373	374
Delaware Sample No.	CO29(S)	CO30(S)	CO31(S)	CO32(S)	CO33(S)	CO34(S)	CO35(S)	CO36(S)	CO37(S)
Ultimate, wt%									
C	22.21	15.87	17.80	18.71	18.03	17.47	57.23	42.88	24.03
H	1.00	0.82	0.94	0.83	0.81	0.76	2.31	1.50	1.14
N	0.51	0.42	0.44	0.45	0.41	0.44	1.06	0.71	0.58
S	5.51	6.29	6.07	5.98	5.84	5.76	3.20	4.34	5.86
Ash	71.56	76.73	74.78	74.99	75.62	76.00	38.71	55.94	67.71
O (by difference)	-1.00	-0.25	-0.15	-1.17	-0.90	-0.67	-2.51	-5.50	0.51
Ash Elementals, wt% of ash									
MoO_3	13.54	14.73	14.46	13.49	13.50	13.51	0.01	0.01	13.53
NiO	2.35	2.83	2.75	2.51	2.55	2.55	0.01	0.01	2.61
SiO_2	5.00	1.99	2.21	4.28	4.50	4.10	23.43	23.19	3.54
Al_2O_3	56.15	62.24	61.30	56.74	57.53	57.82	12.77	12.48	58.70
TiO_2	0.25	0.14	0.17	0.23	0.23	0.25	0.94	0.92	0.21
Fe_2O_3	4.59	1.80	2.37	4.18	4.11	4.03	20.93	20.66	3.44
CaO	2.93	1.22	1.58	2.75	2.65	2.61	14.02	13.80	2.29
MgO	0.67	0.26	0.35	0.61	0.63	0.61	3.38	3.26	0.53
Na_2O	0.39	0.17	0.23	0.35	0.37	0.35	1.85	1.79	0.32
K_2O	0.10	0.04	0.05	0.08	0.08	0.08	0.42	0.45	0.08
P_2O_5	6.73	7.26	7.02	6.36	6.37	6.43	0.59	0.59	6.62
SO_3	4.20	1.31	1.88	3.56	3.33	3.44	20.17	19.84	2.79
Unaccounted	3.11	6.01	5.63	4.87	4.16	4.23	1.48	3.00	5.35

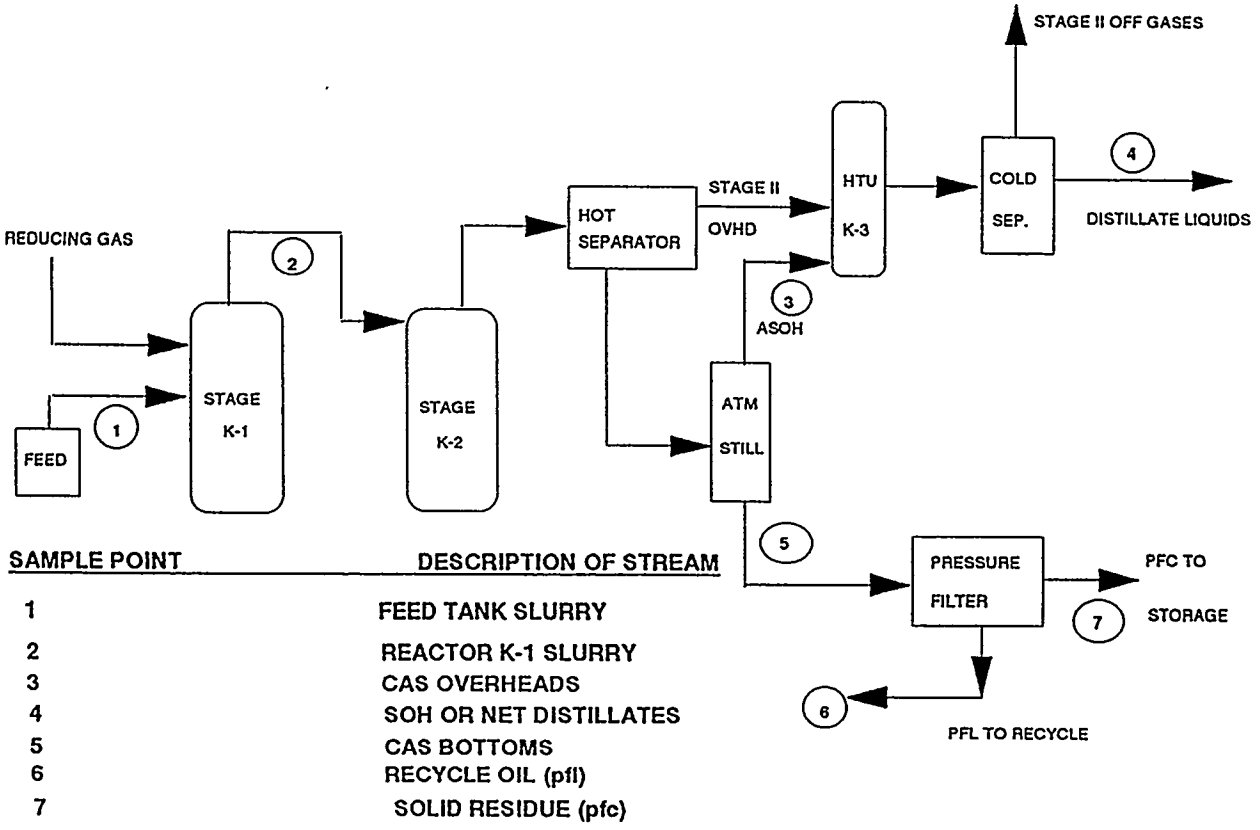


Figure 1. Simplified Plant Diagram for HTI Run CMSL-8.
(Source: Reference 1)

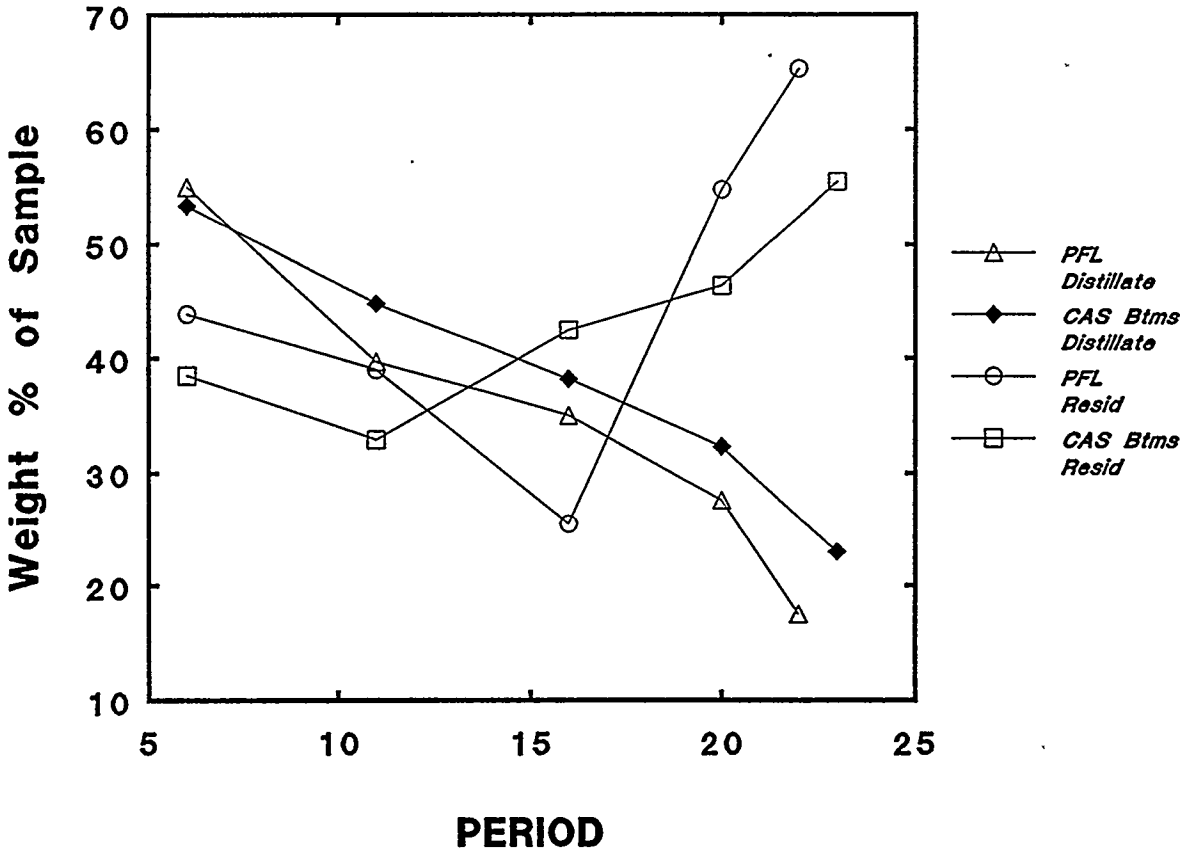


Figure 2. Distillate and Resid Content of Selected Process Streams During HTI Run CMSL-8.

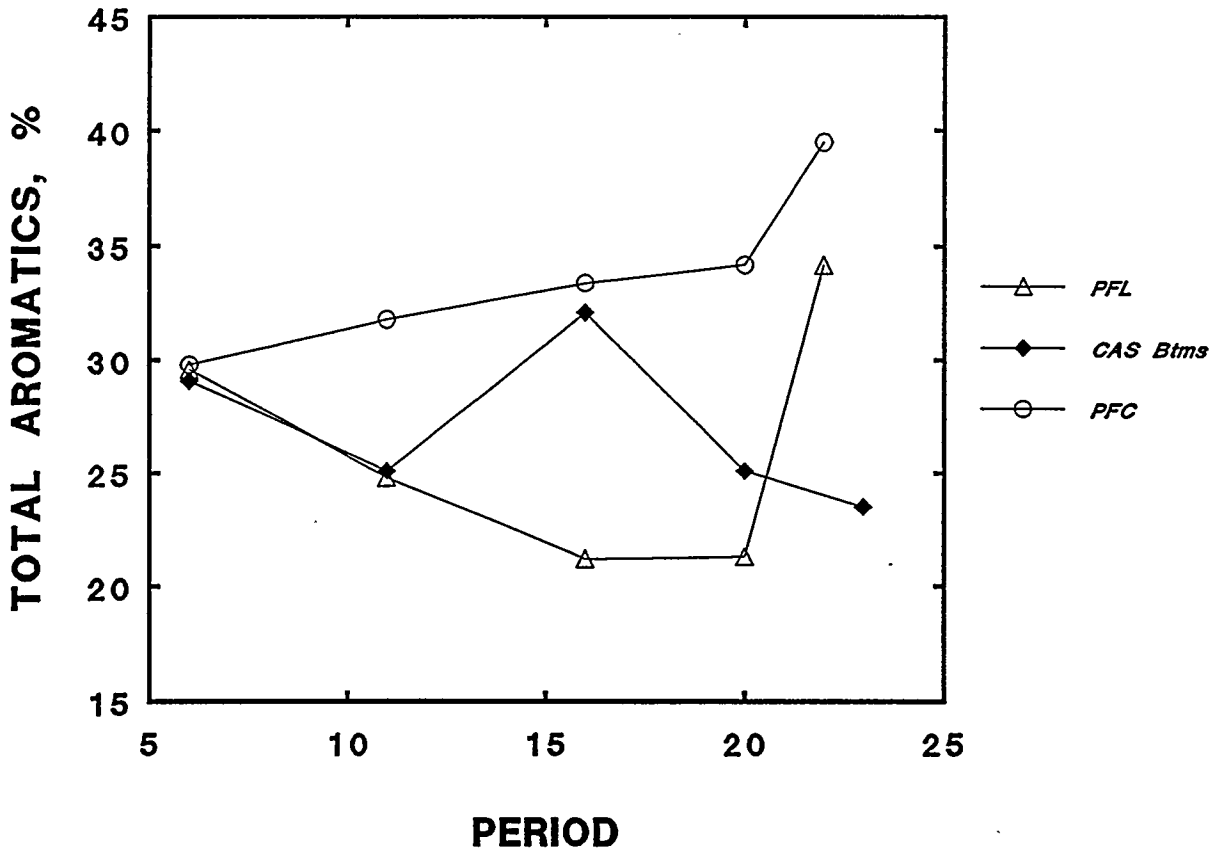


Figure 3. Proton Aromaticity of Whole Process Stream Samples During HTI Run CMSL-8.

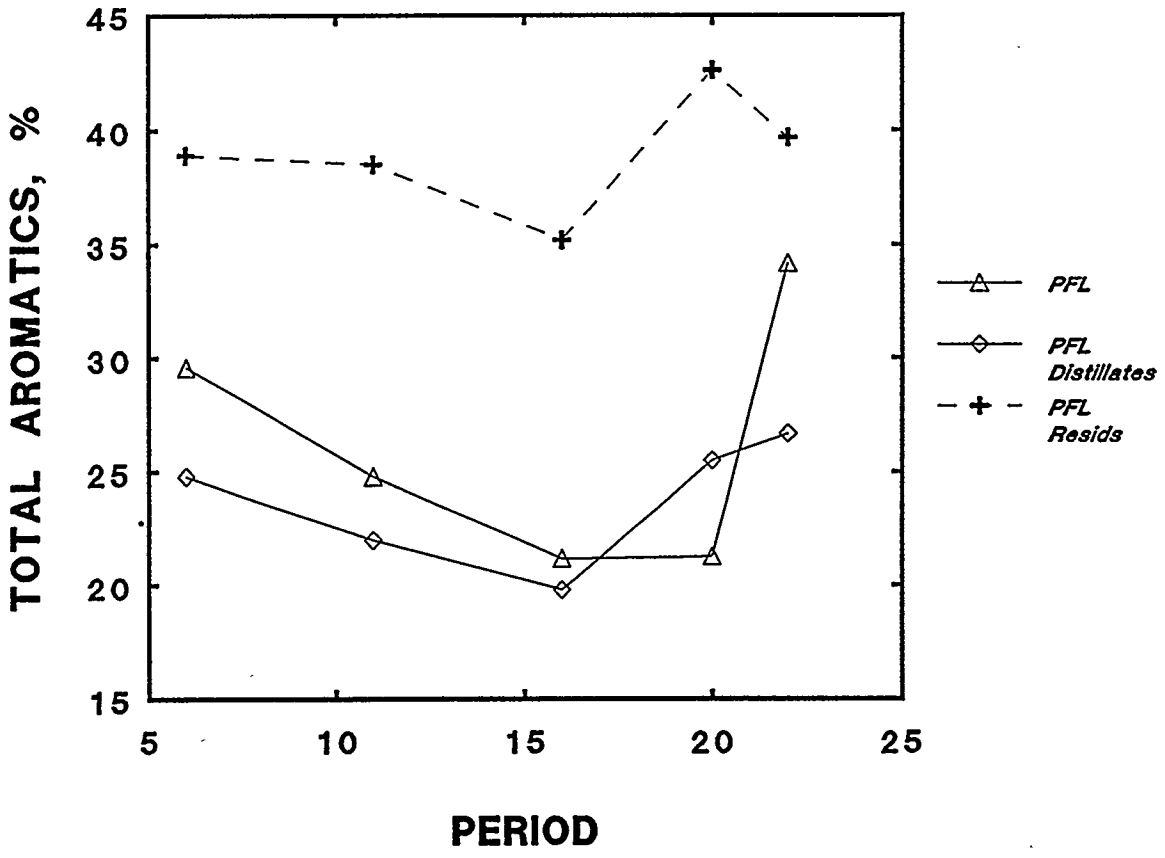


Figure 4. Proton Aromaticity of the Whole PFL, PFL Distillate and PFL Resid Samples During HTI Run CMSL-8.

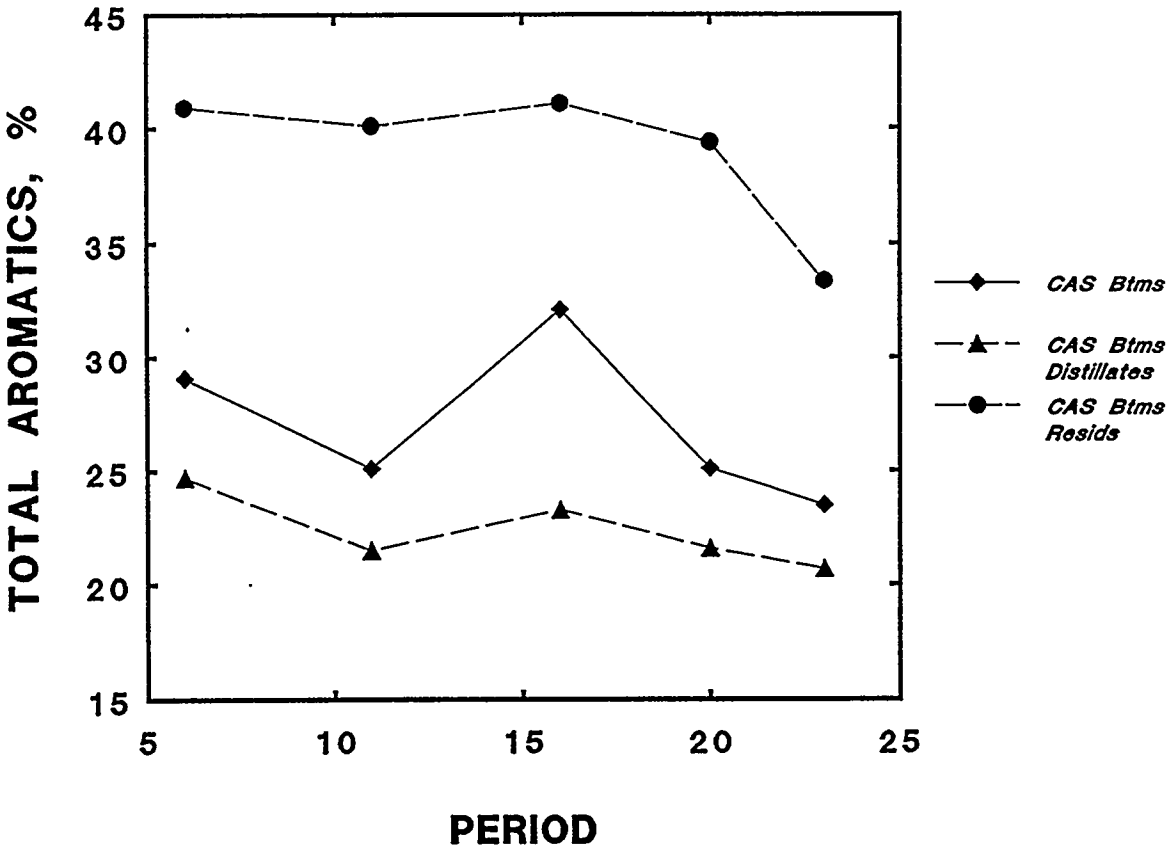


Figure 5. Proton Aromaticity of the Whole CAS Bottoms, CAS Bottoms Distillate and CAS Bottoms Resid Samples During HTI Run CMSL-8.

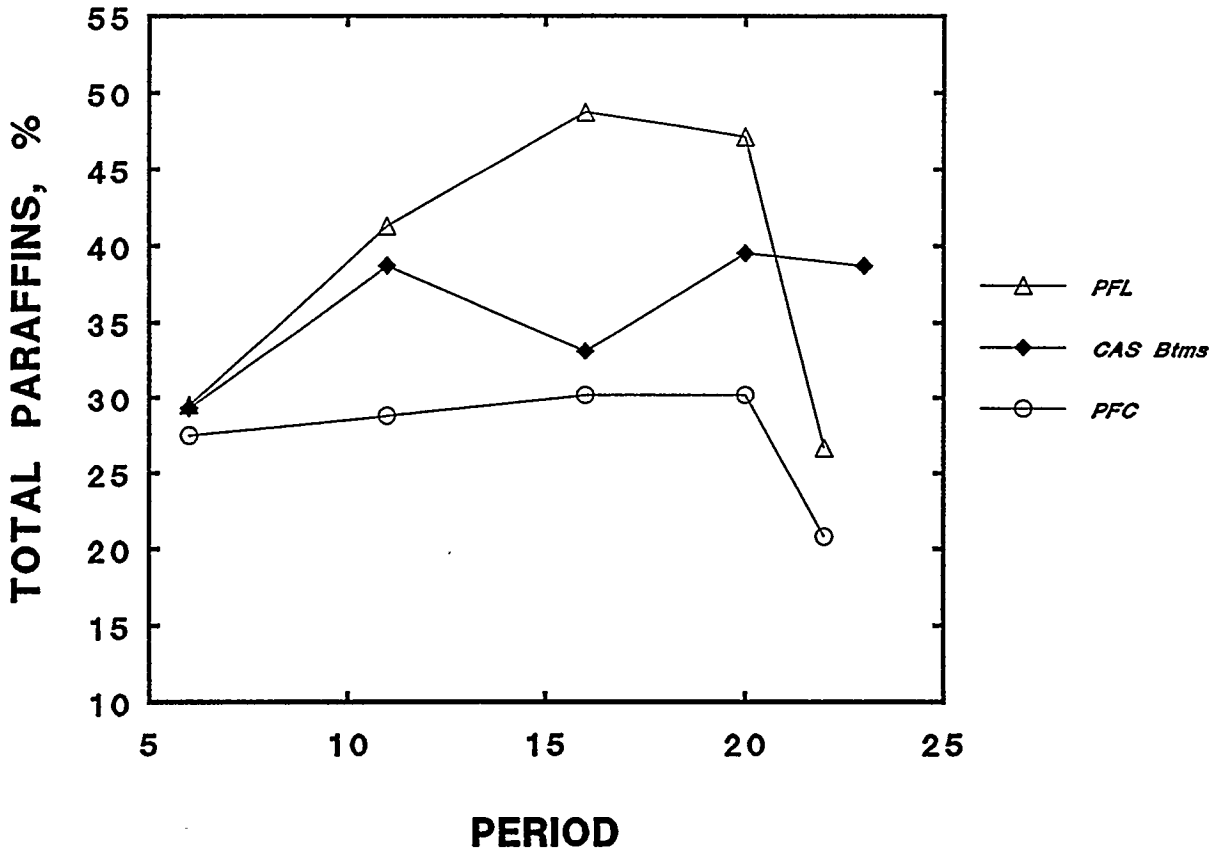


Figure 6. Proton Paraffinicity of Whole Process Stream Samples During HTI Run CMSL-8.

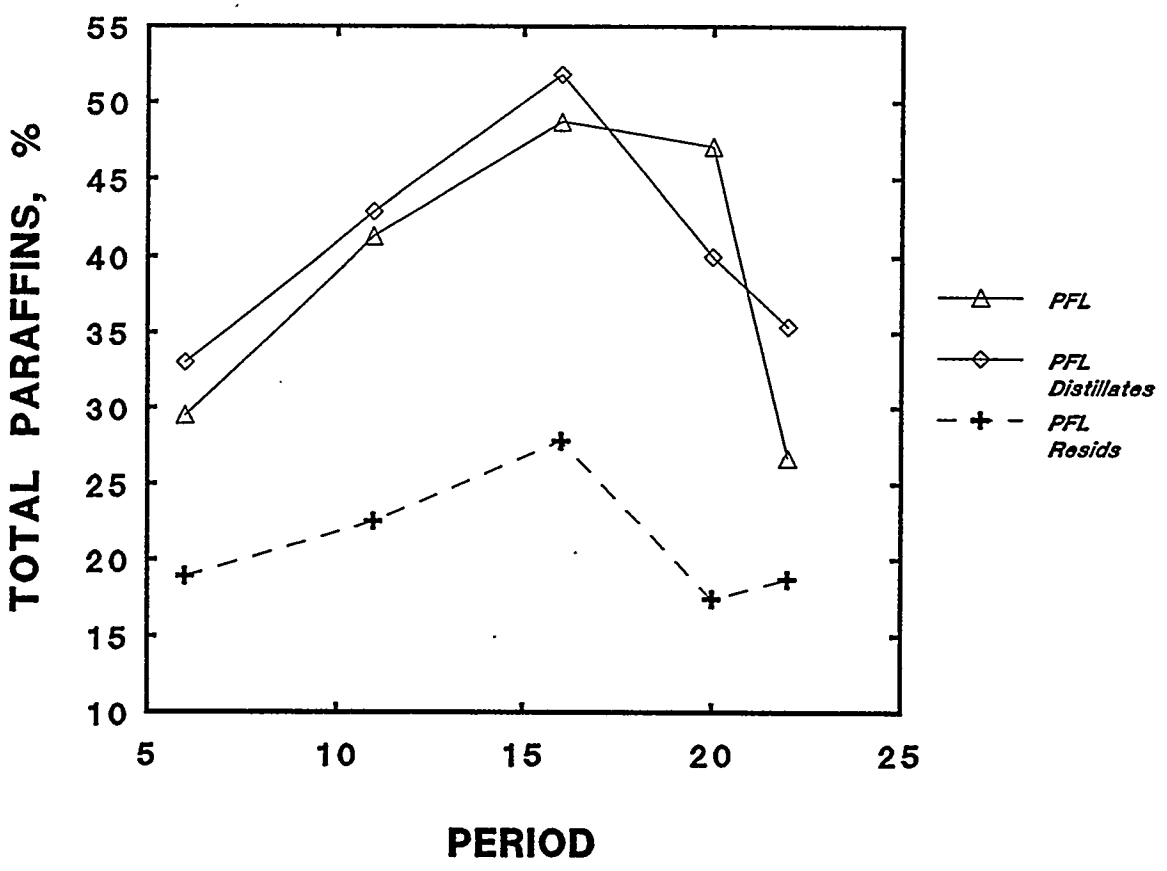


Figure 7. Proton Paraffinicity of the Whole PFL, PFL Distillate and PFL Resid Samples During HTI Run CMSL-8.

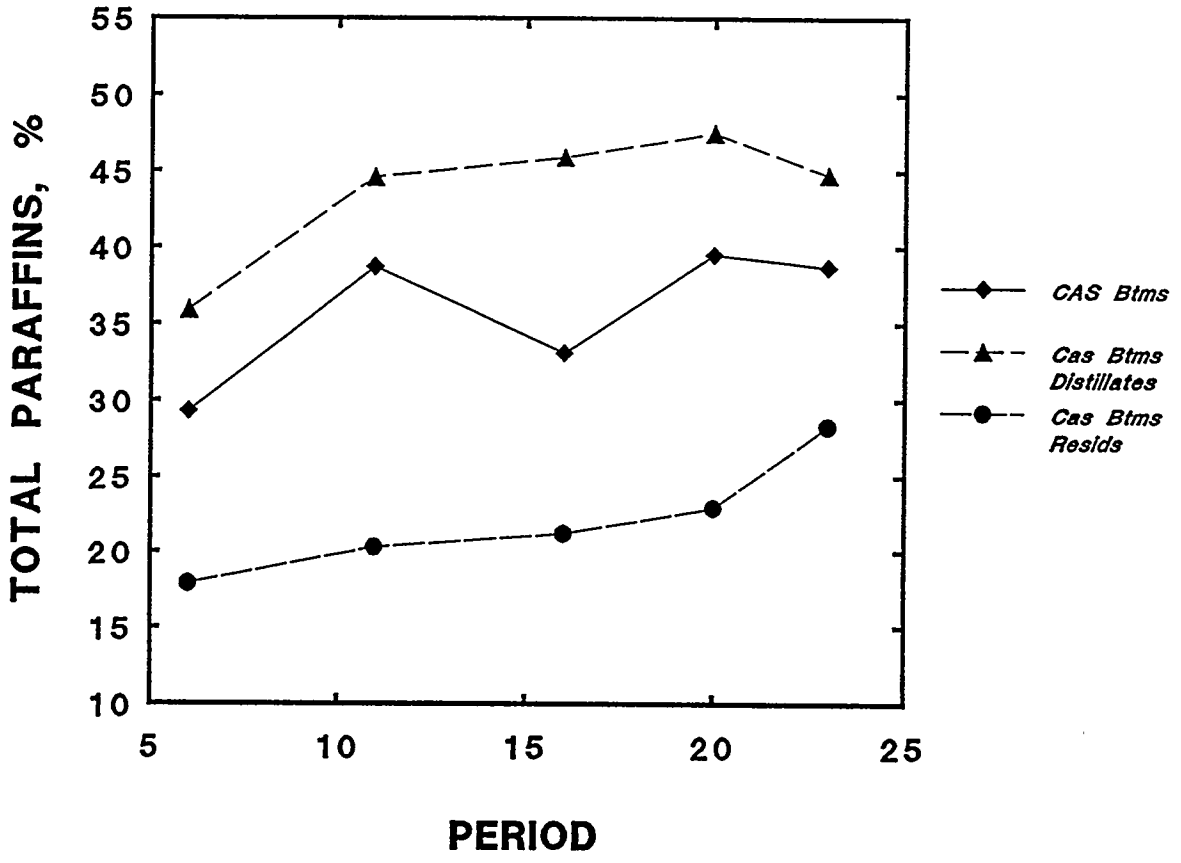


Figure 8. Proton Paraffinicity of the Whole CAS Bottoms, CAS Bottoms Distillate and CAS Bottoms Resid Samples During HTI Run CMSL-8.

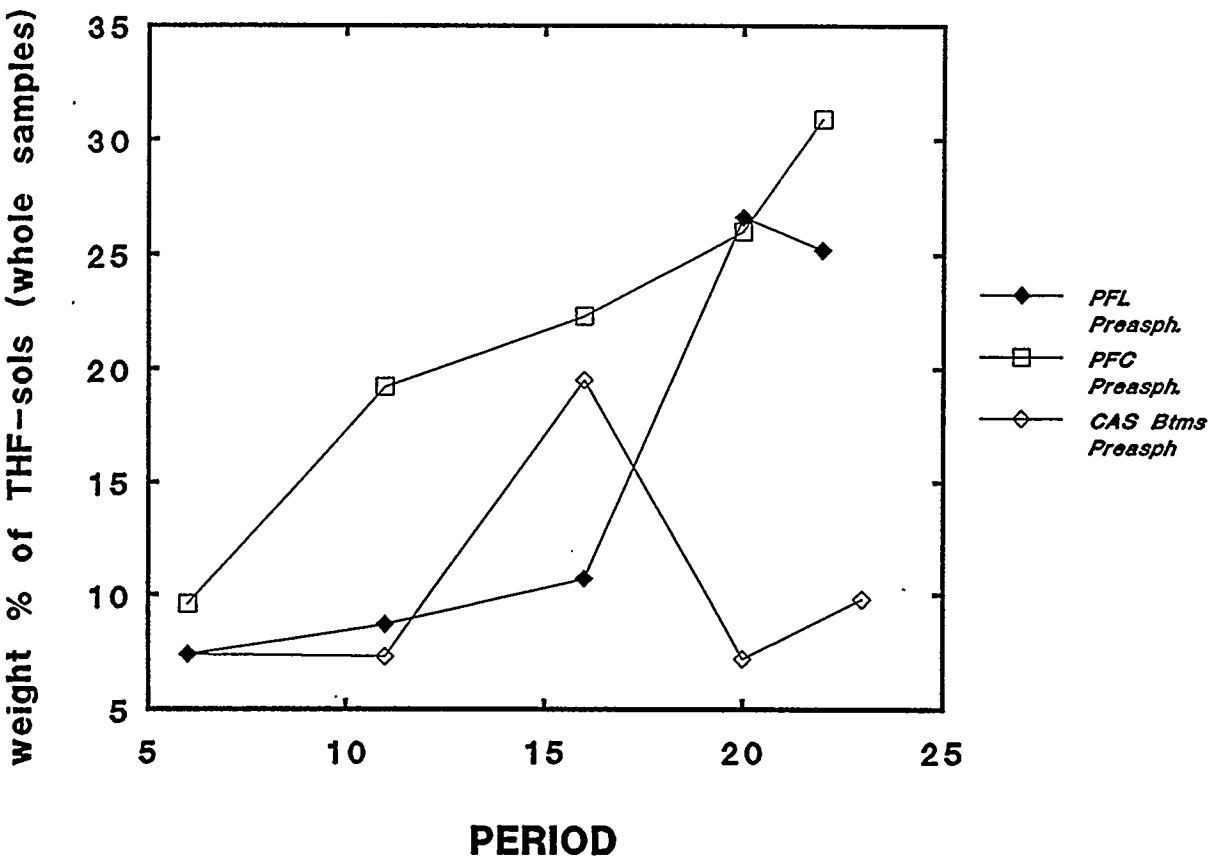


Figure 9. Preasphaltene Content of THF Extracts from Whole Samples.

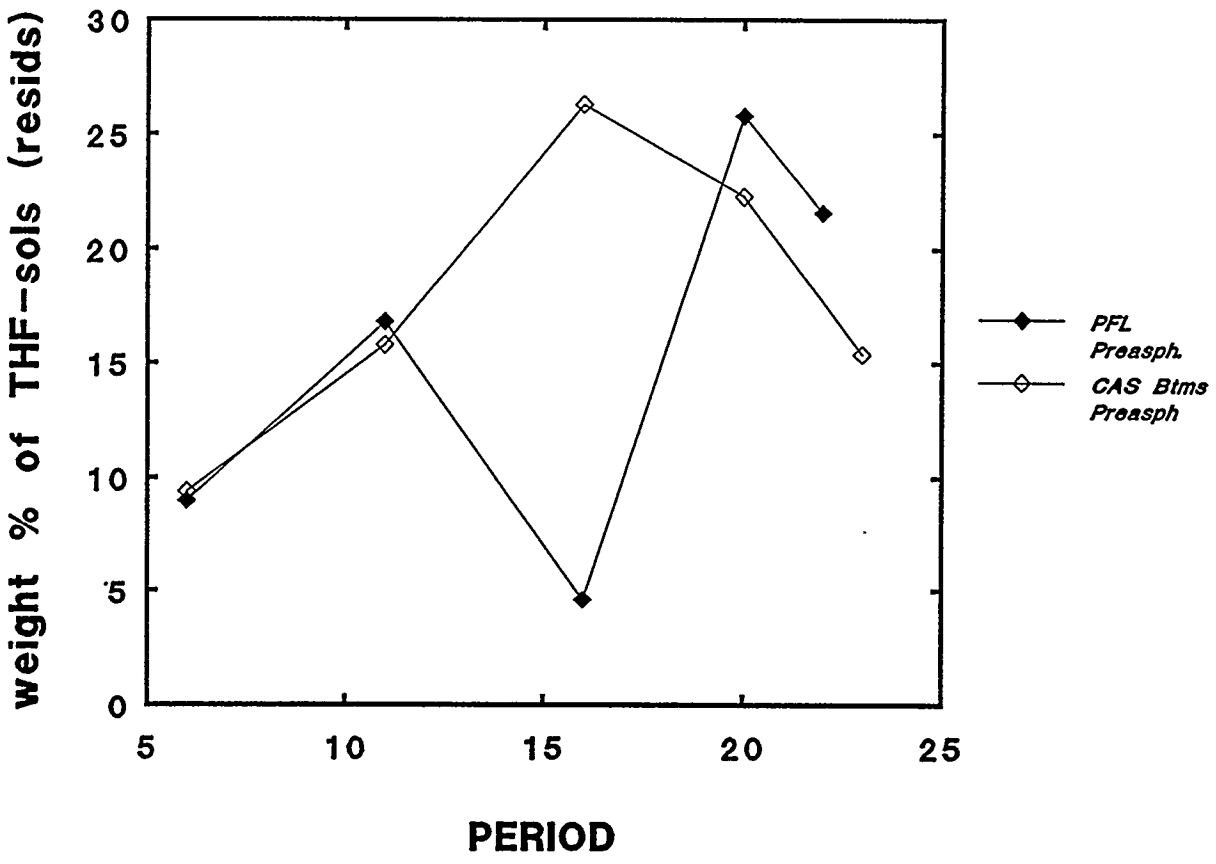


Figure 10. Preasphaltene Content of THF Extracts from Resid Samples.

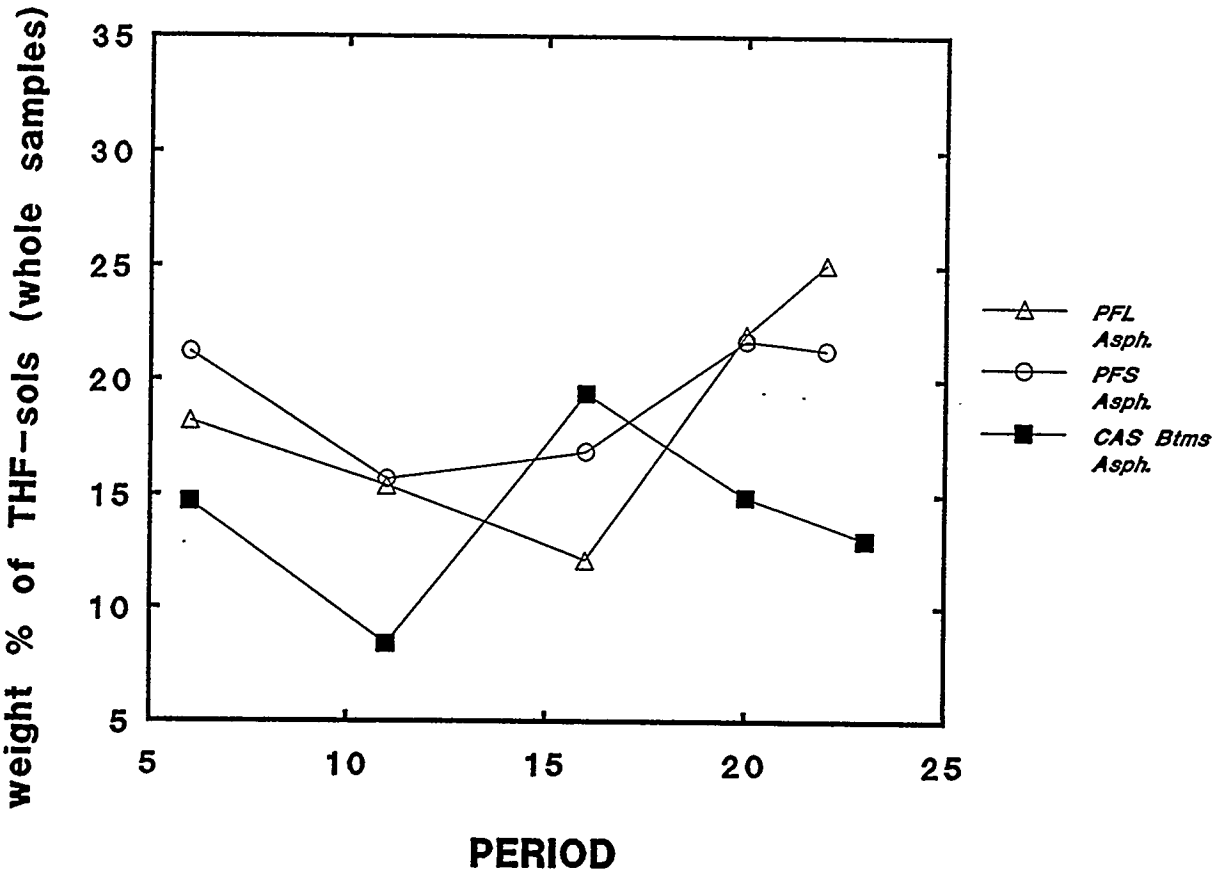


Figure 11. Asphaltene Content of THF Extracts from Whole Samples.

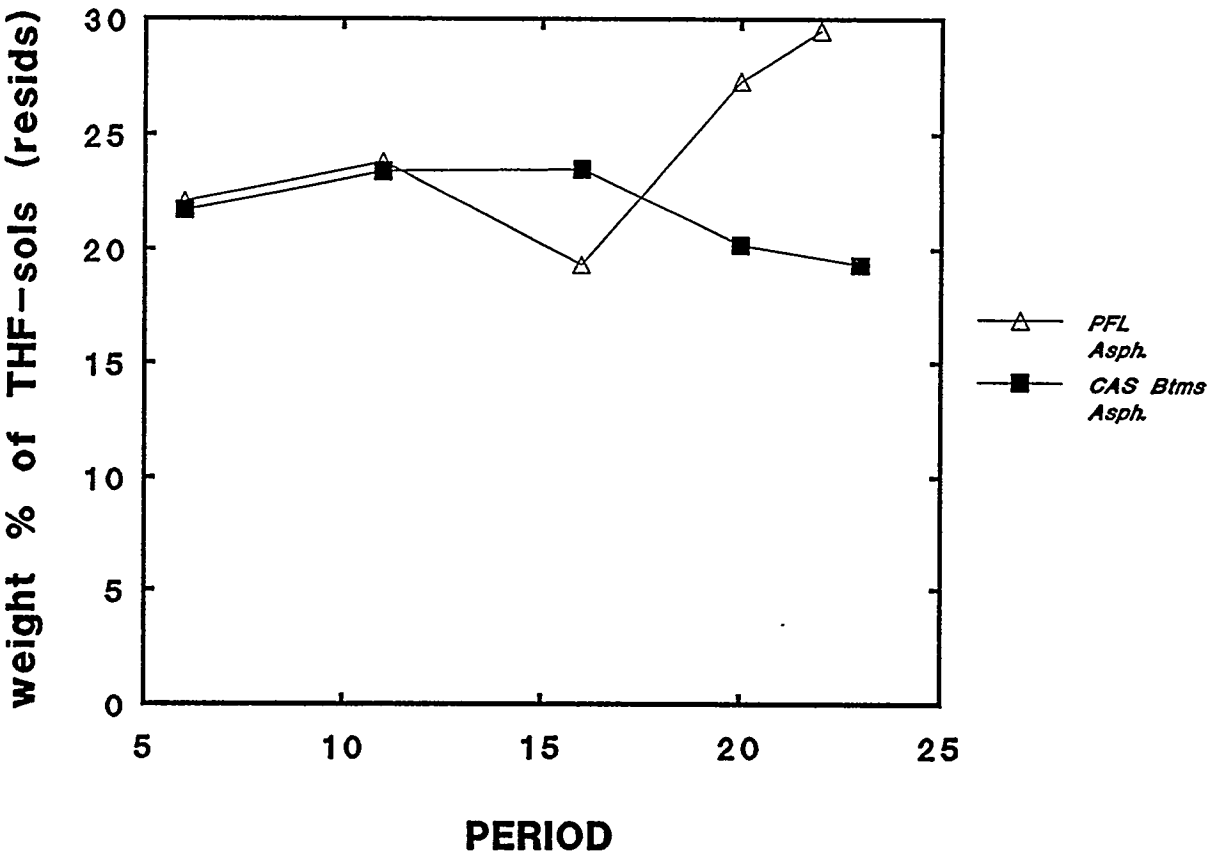


Figure 12. Asphaltene Content of THF Extracts from Resid Samples.

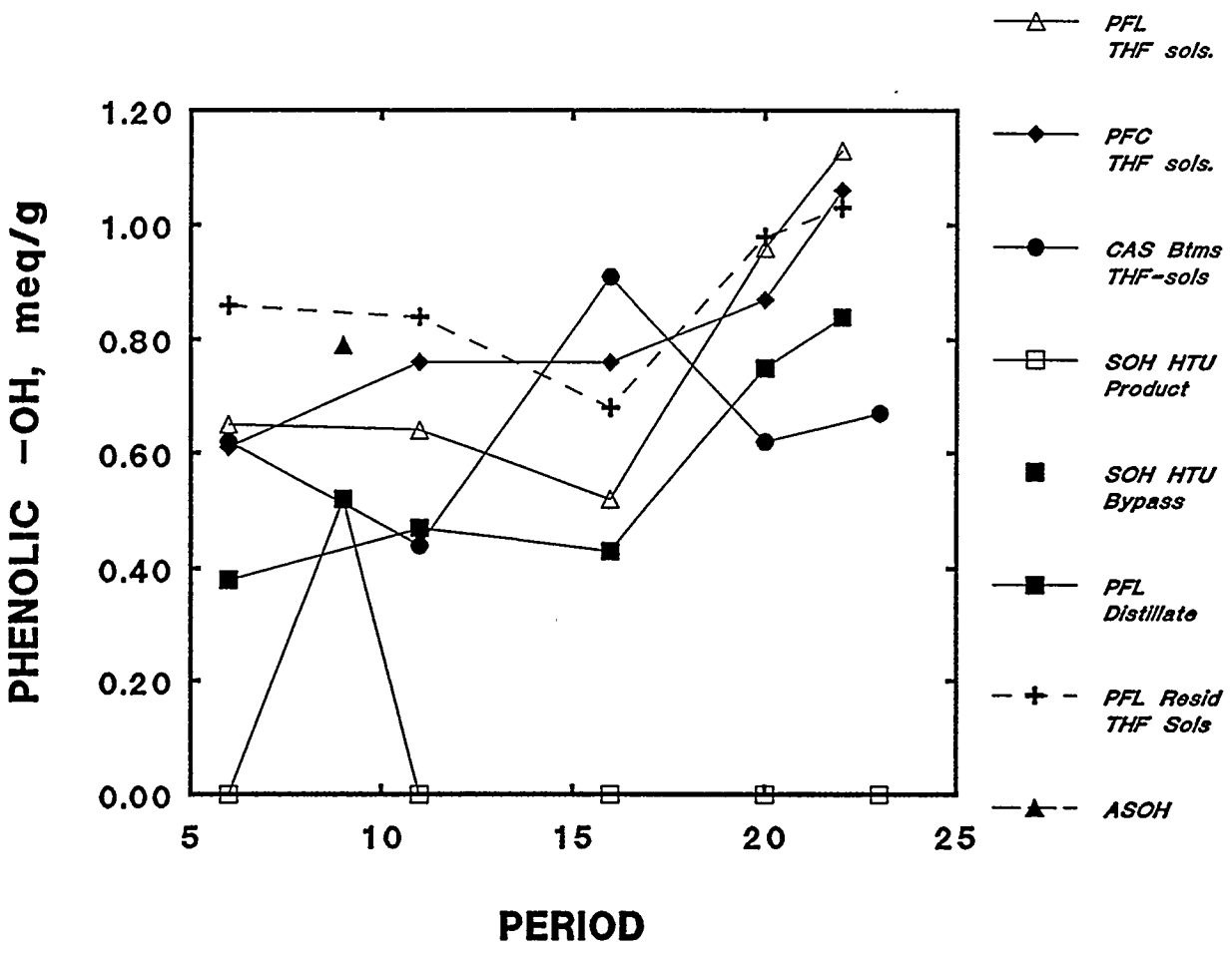


Figure 13. Phenolic -OH Concentration of Process Stream Samples During HTI Run CMSL-8.

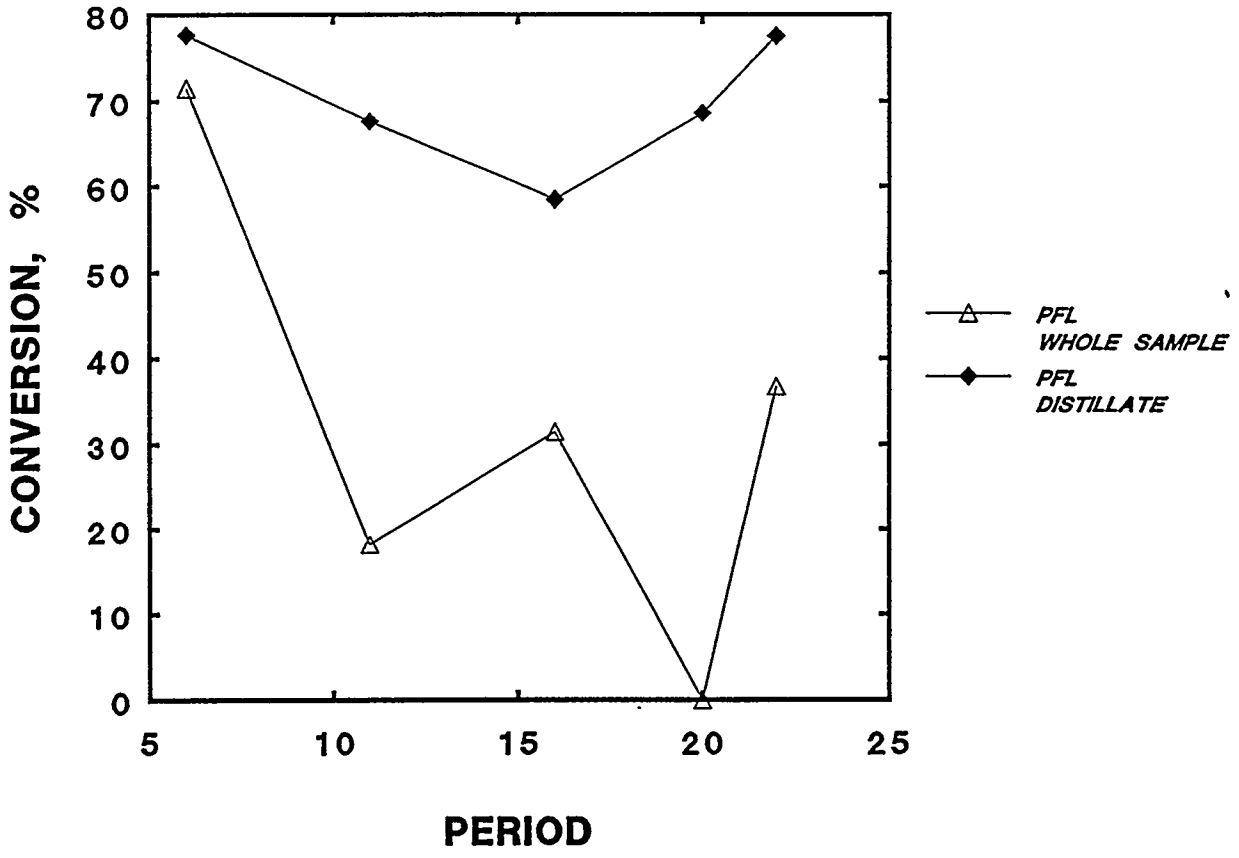


Figure 14. Donor Solvent Quality of Whole PFL and PFL Distillate Samples During HTI Run CMSL-8.

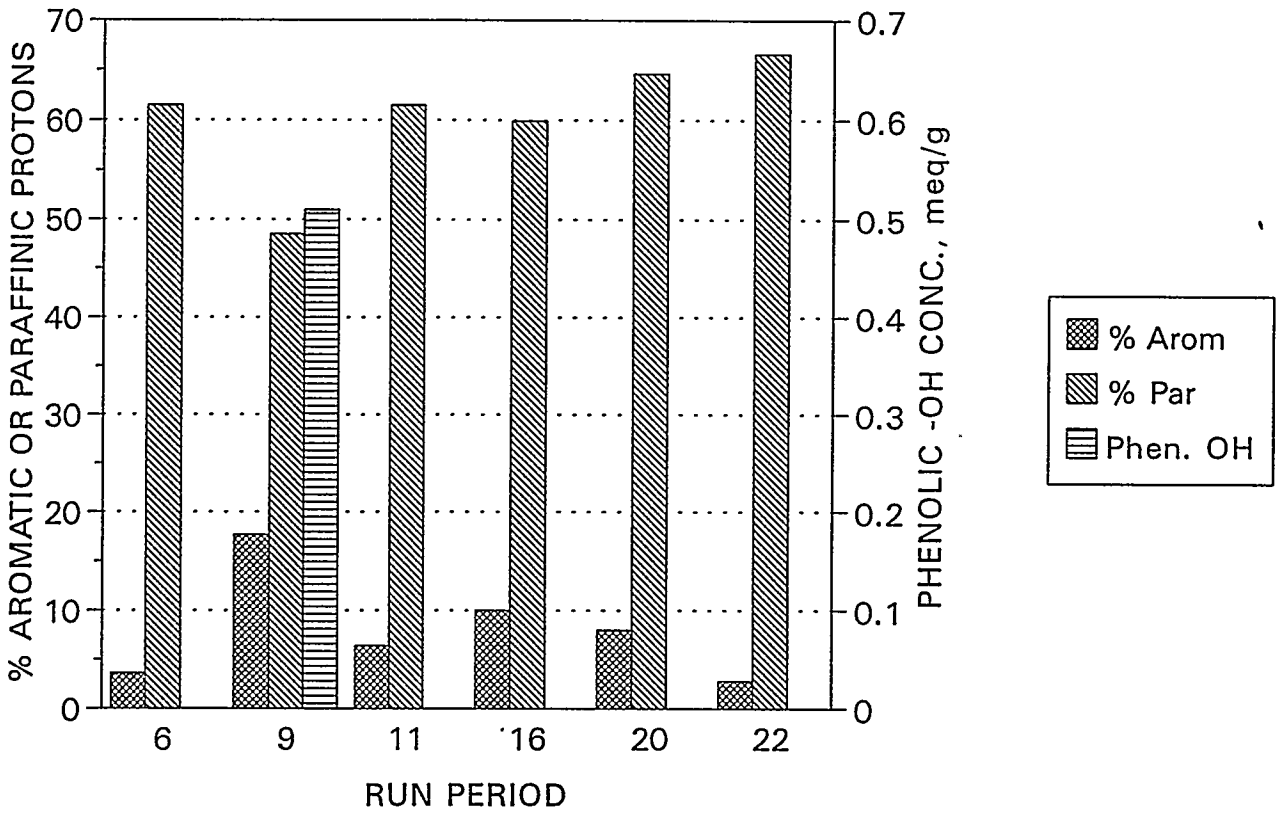


Figure 15. Characteristics of SOH Samples from Run CMSL-8.

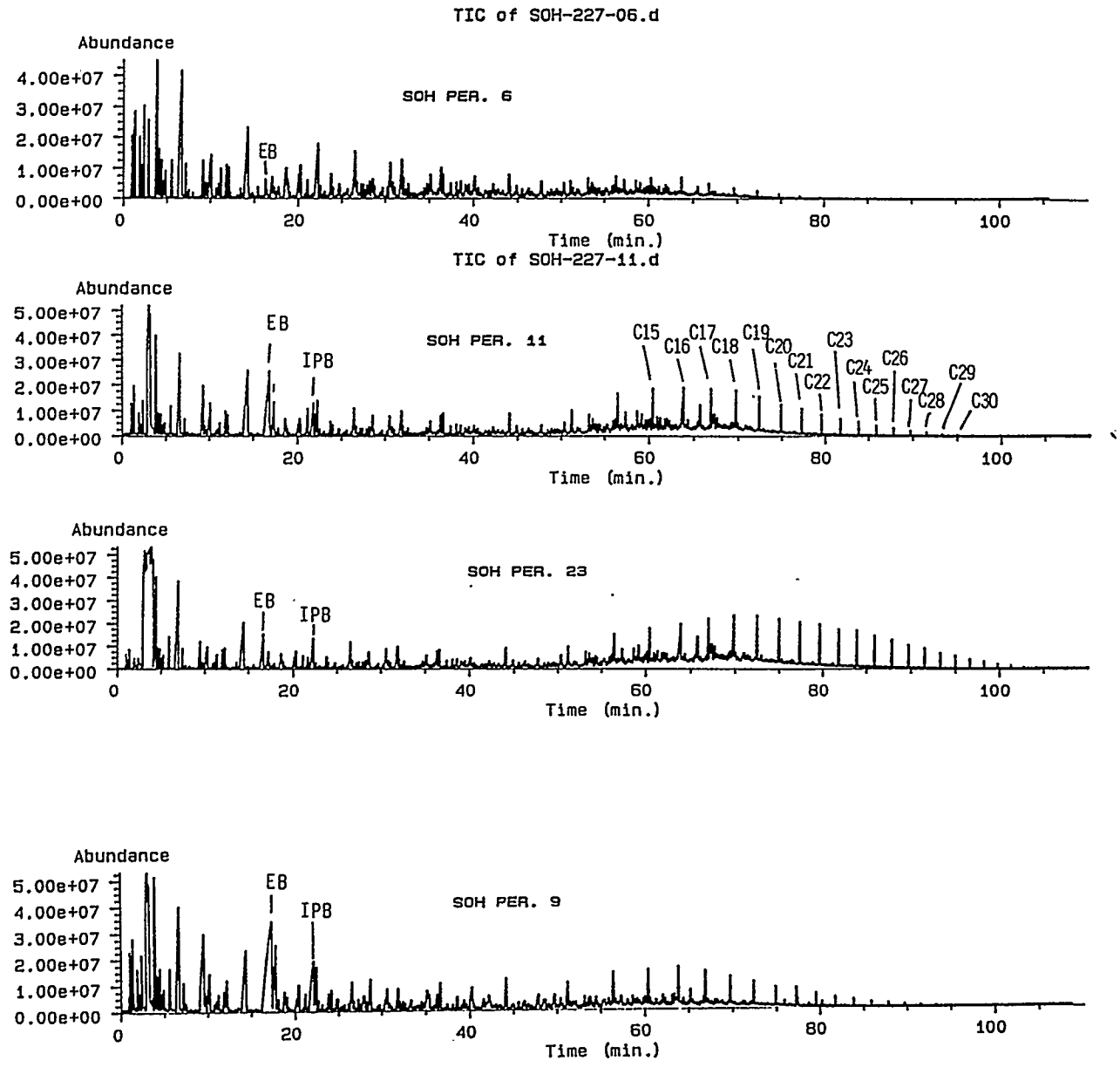


Figure 16. Gas Chromatography-Mass Spectrometry (GC-MS) Total Ion Chromatograms of Selected SOH Samples from Run CMSL-8.

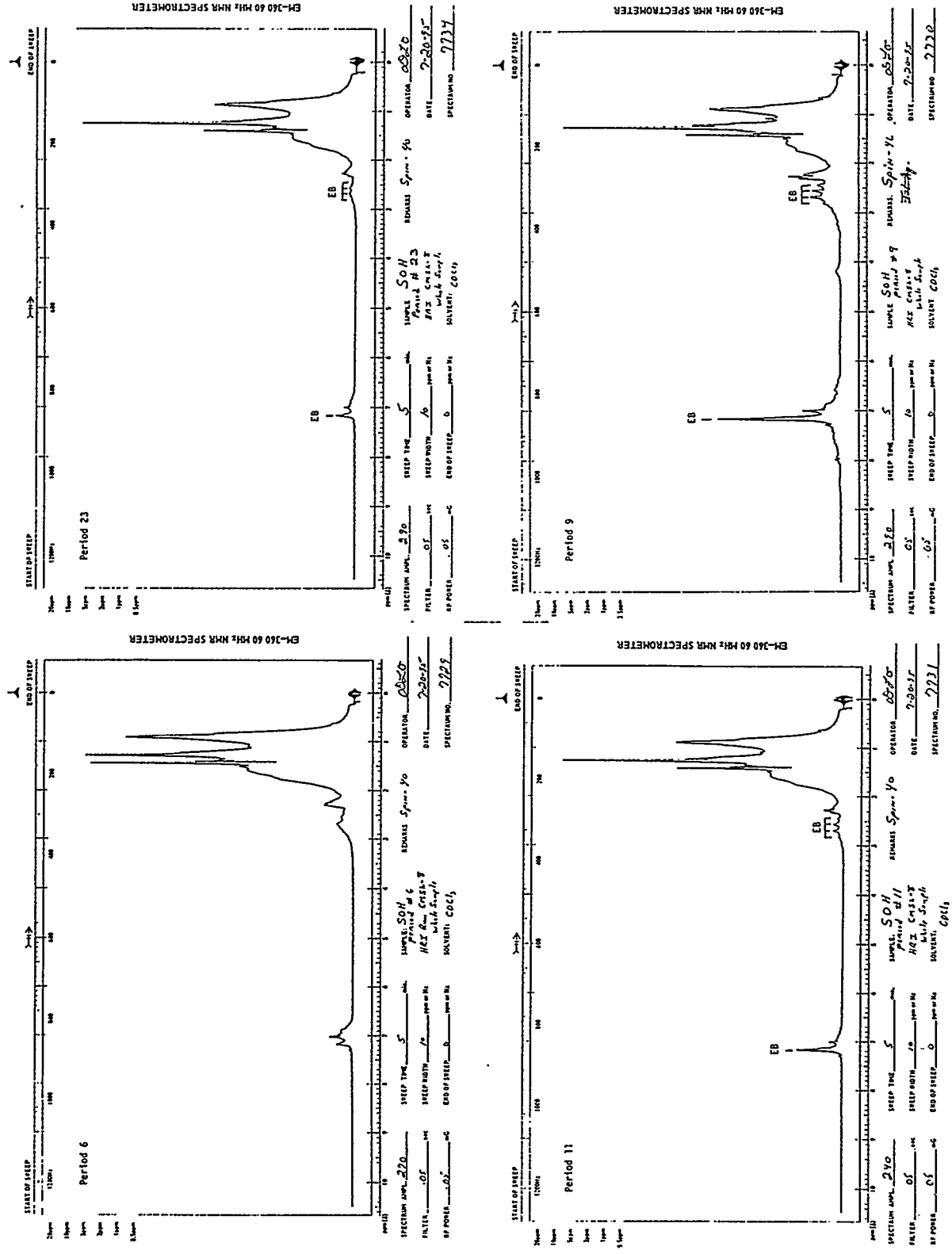


Figure 17. Proton NMR Spectra of Selected SOH Samples.

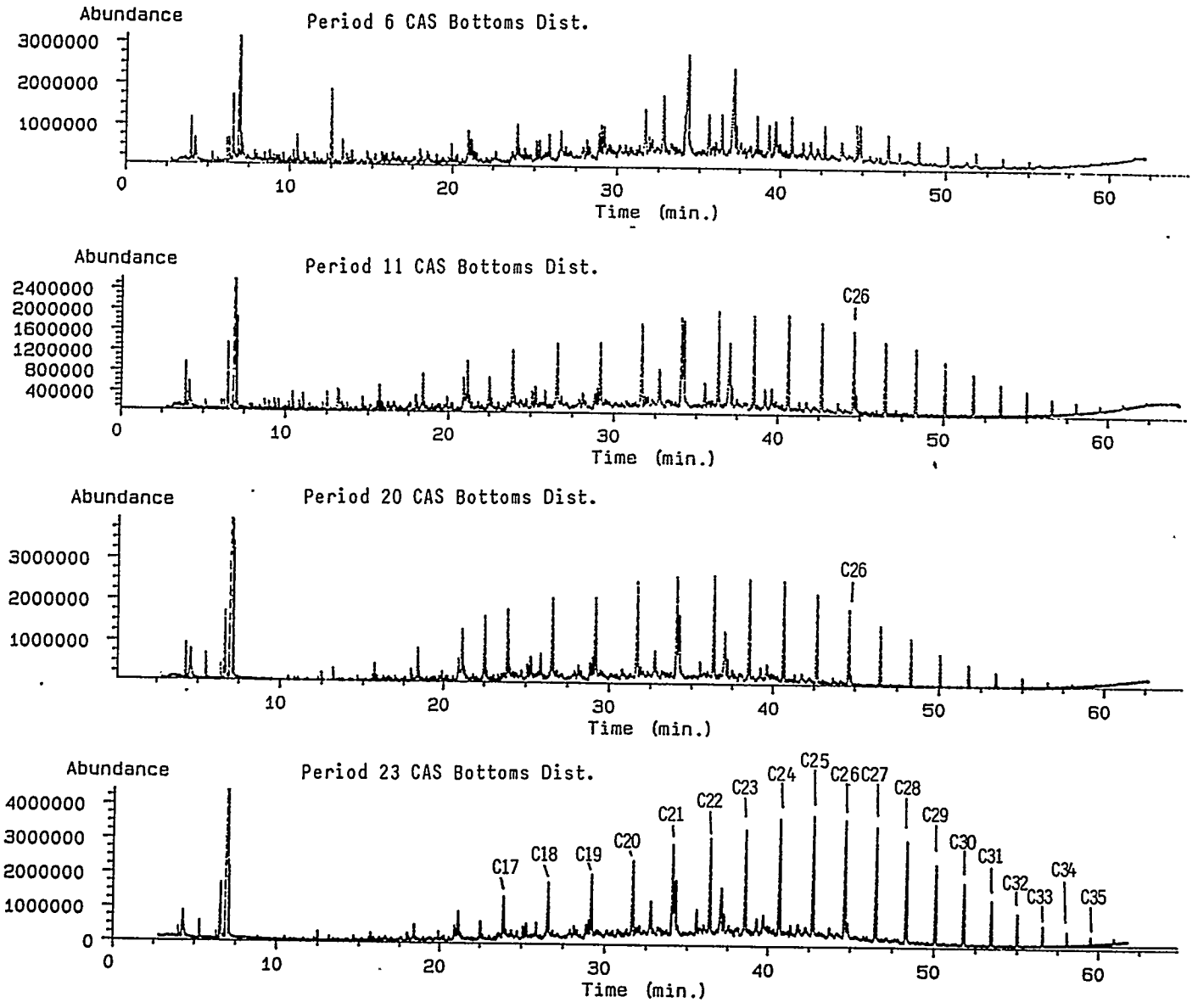
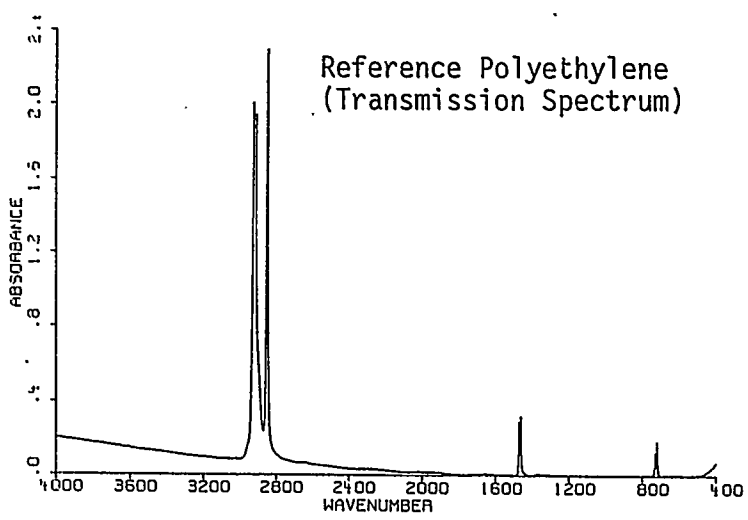
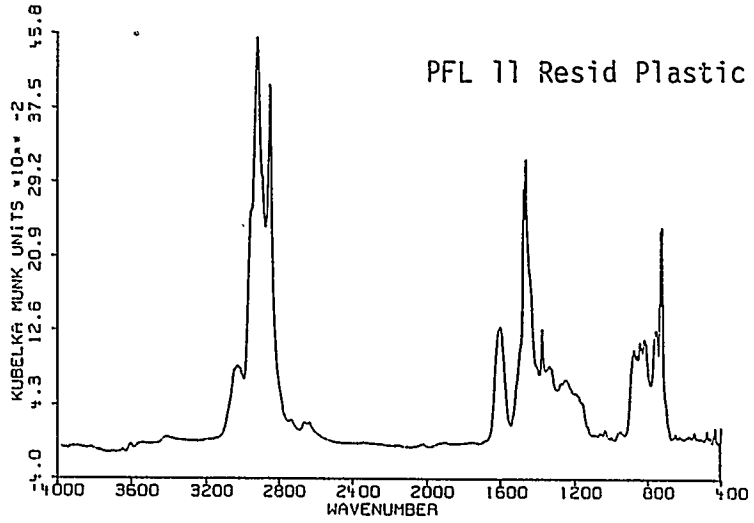
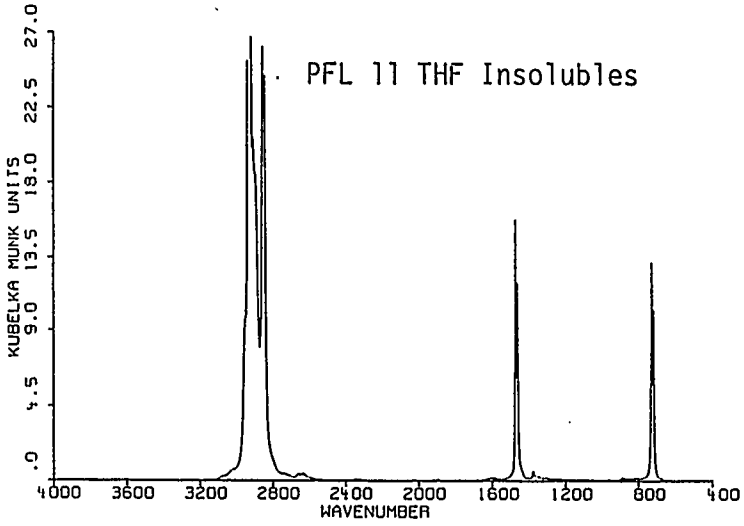


Figure 18. Gas Chromatography-Mass Spectrometry (GC-MS) Total Ion Chromatograms of Selected CAS Bottoms Distillate Samples from Run CMSL-8.







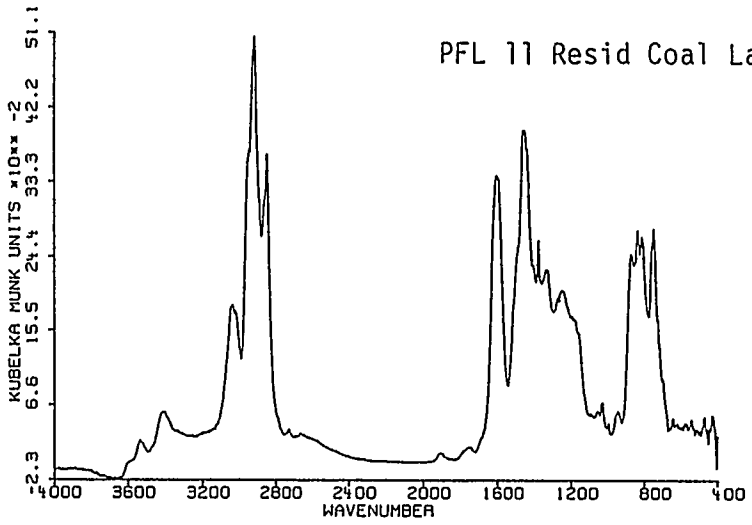


Figure 19. Fourier-Transform Infrared (FTIR) Spectra of Reference Polyethylene and Selected Run CMSL-8 Samples.

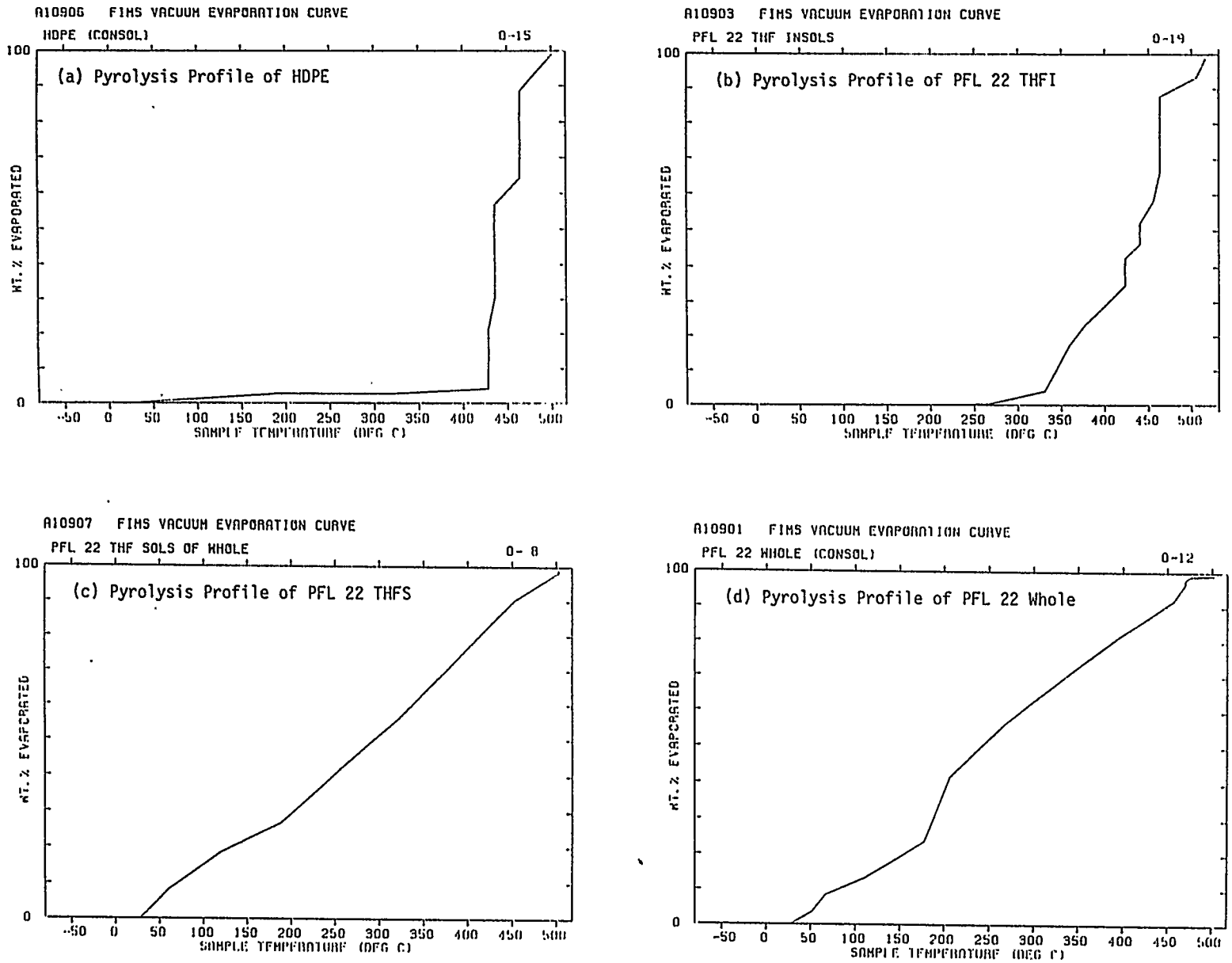


Figure 20. Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

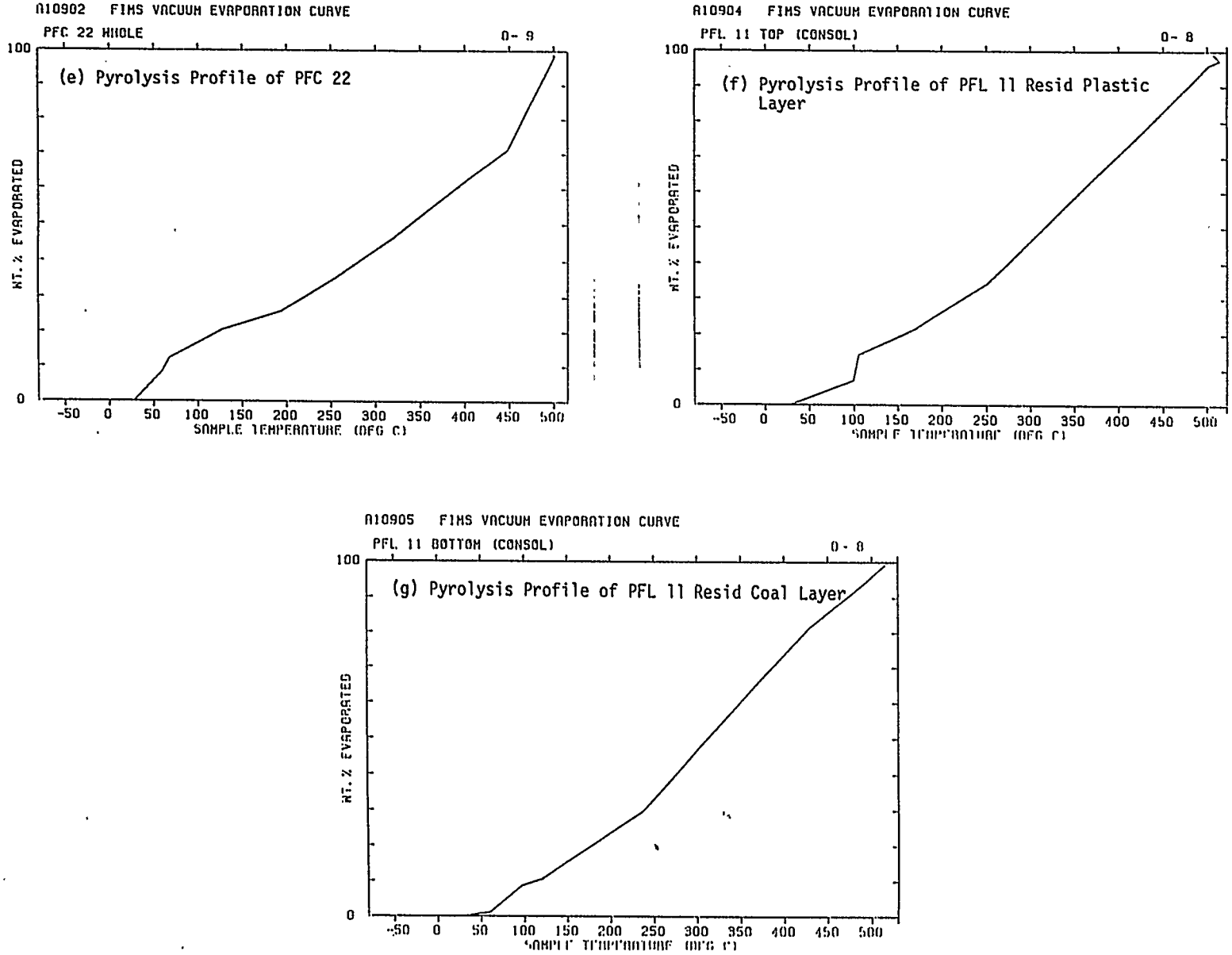


Figure 20 (Cont'd). Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

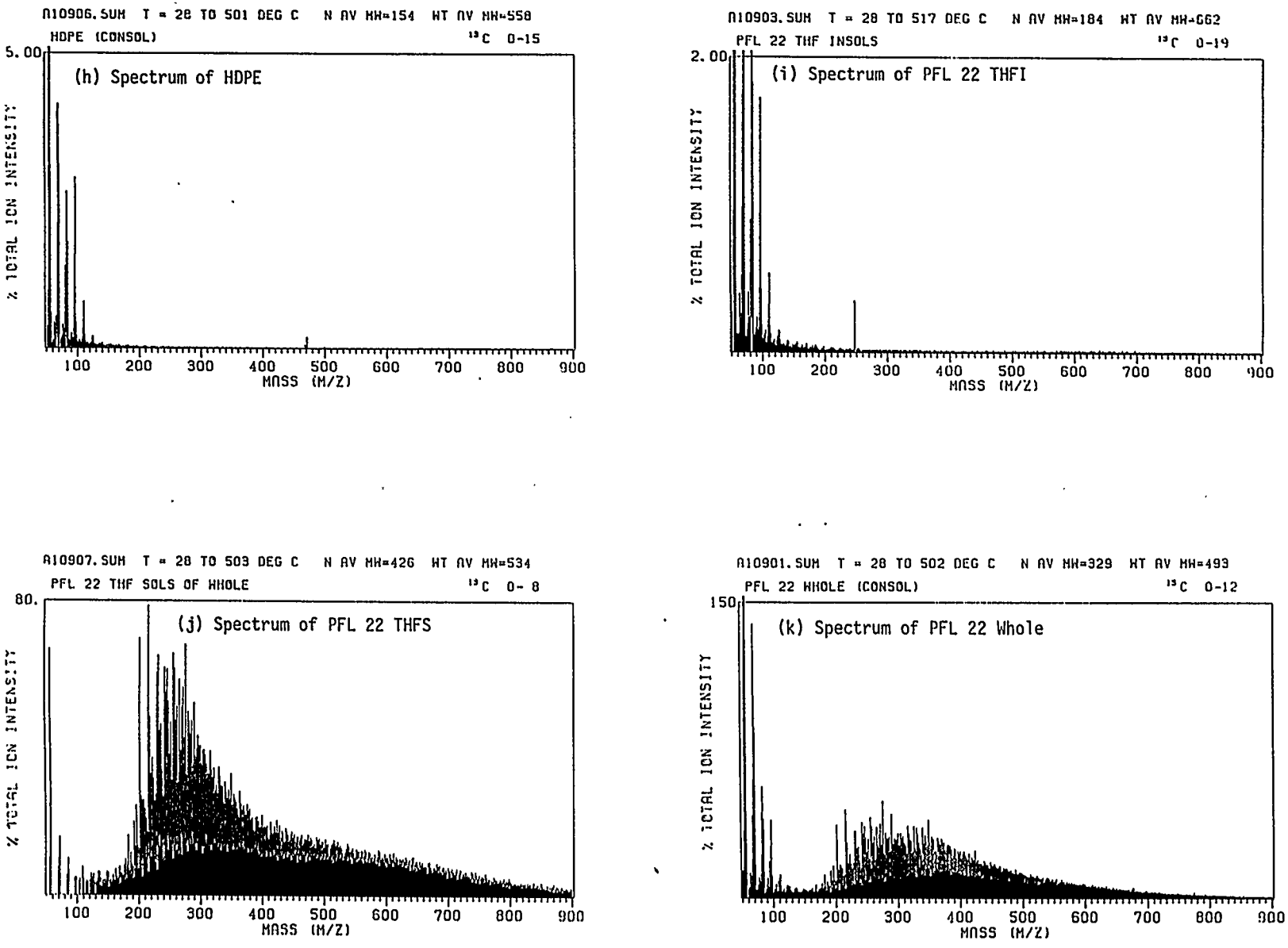


Figure 20 (Cont'd). Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

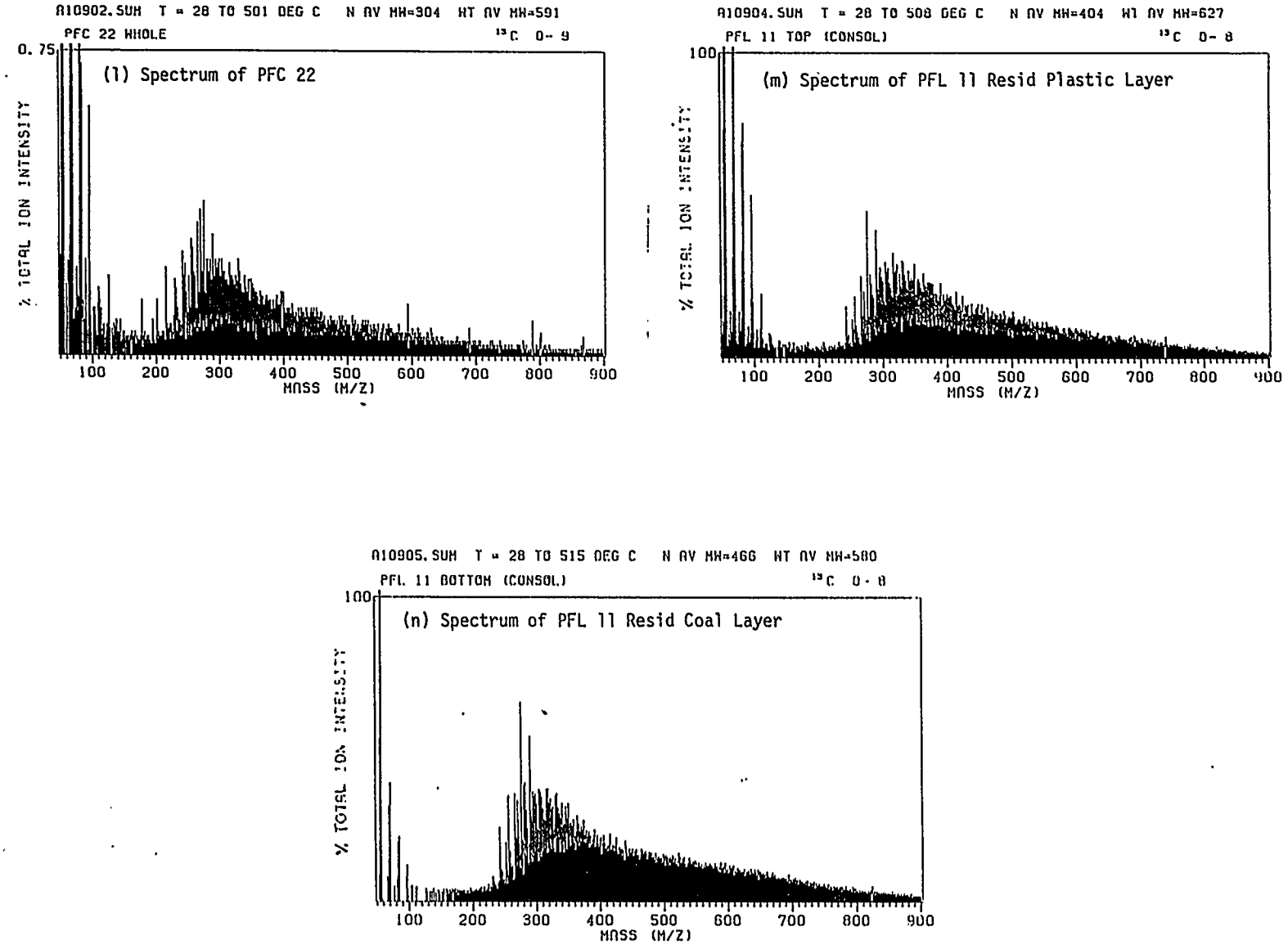


Figure 20 (Cont'd). Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

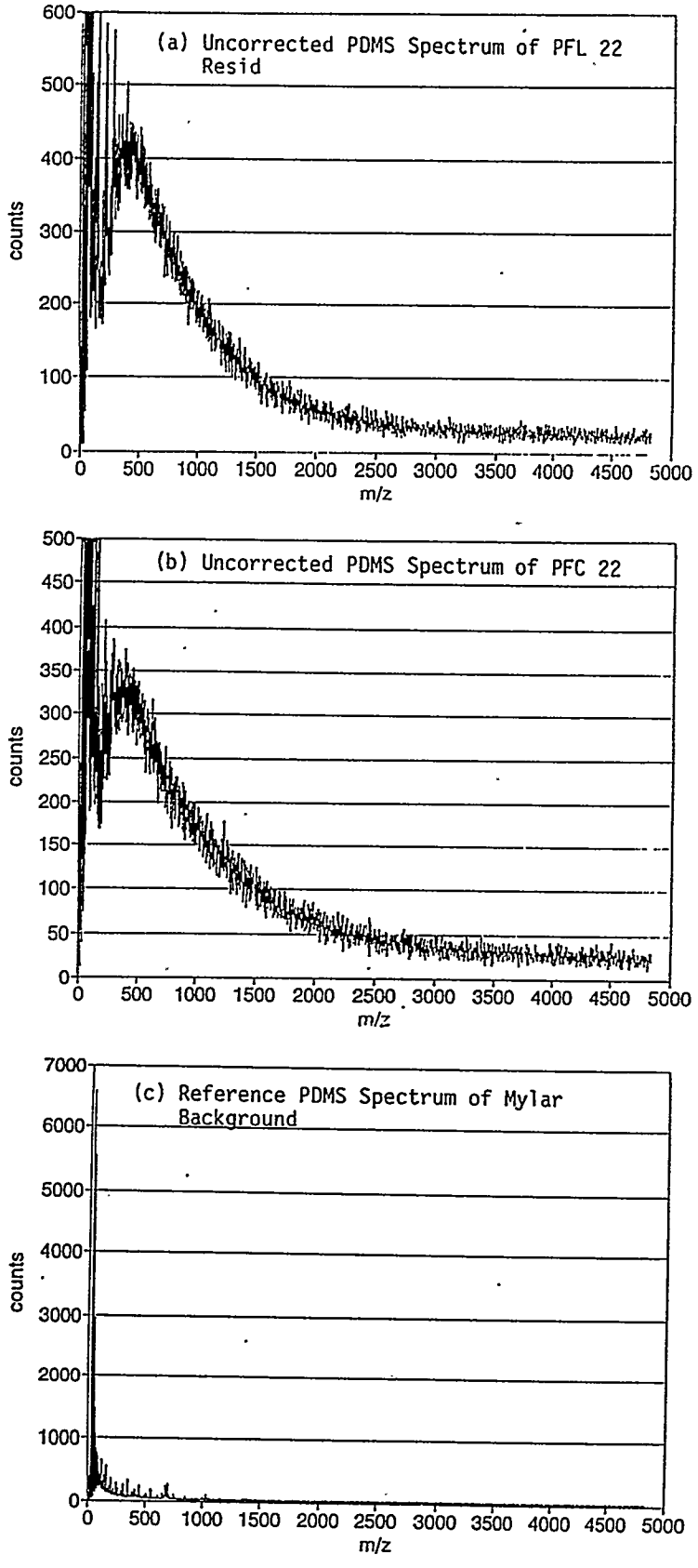


Figure 21. PDMS Spectra of Samples from Coal/Plastics Operations.

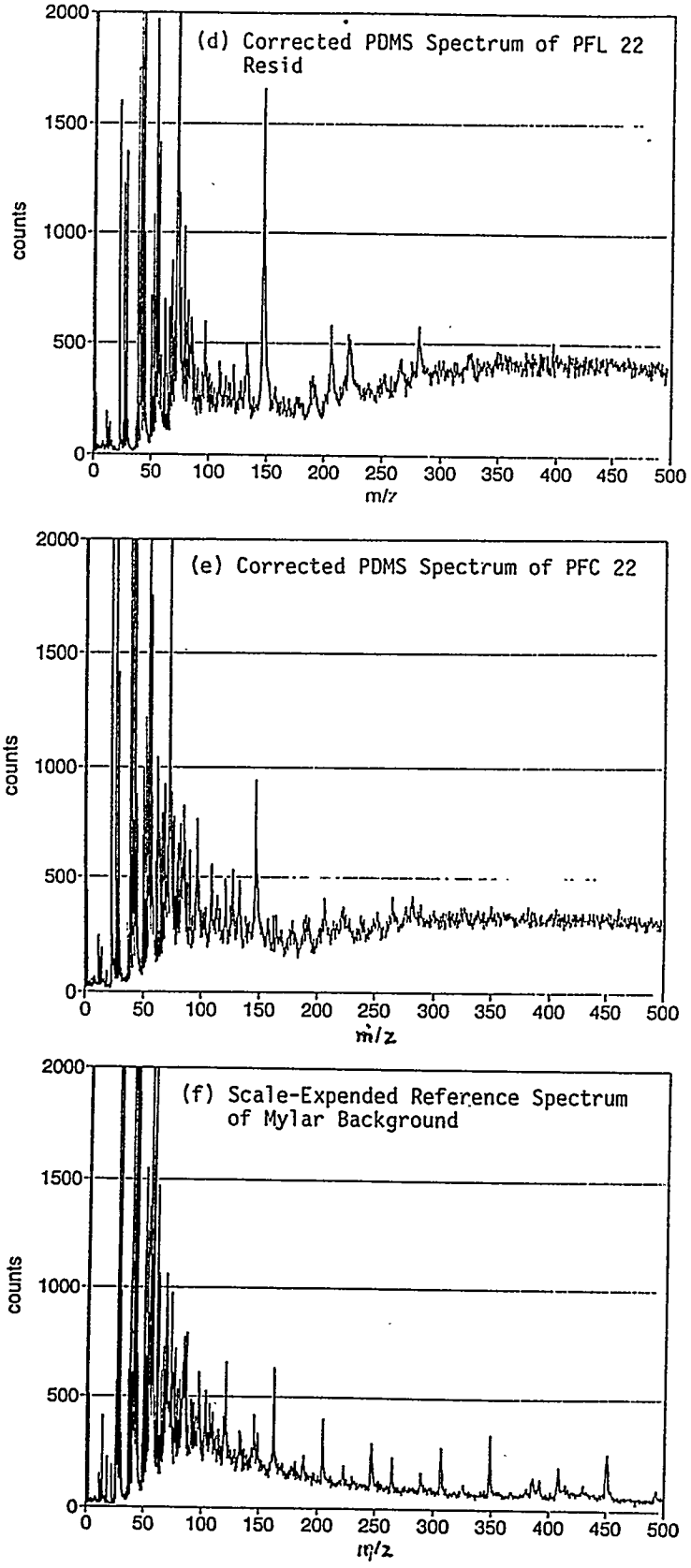


Figure 21 (Cont'd). PDMS Spectra of Samples from Coal/Plastics Operations.

APPENDIX 1

CMSL-9 ANALYTICAL PLAN

SAMPLE ANALYSIS PLAN FOR HTI RUN CMSL-9 (227-87)
COAL: BLACK THUNDER SUBBITUMINOUS

PRINTED: 02:20 PM 09/06/95
LIST UPDATED: 09/06/95

SAMPLES			ANALYSES								X = ANALYSIS PLANNED, SHADED = COMPLETED									LAB #
LQ-#	TYPE	PER.	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	1621-33-
6556	FEED SLURRY	5		X																376
6557	FEED SLURRY	9		X																377
6558	FEED SLURRY	15		X																378
	FEED SLURRY	19B		X																435
	FEED SLURRY	24B		X																430
	FEED SLURRY	29B		X																431
	FEED SLURRY	34B		X																432
	FEED SLURRY	36A		X																433
	FEED SLURRY	41B		X																435
	K-1 SLURRY	19B		X																450
	K-1 SLURRY	24B		X																451
	K-1 SLURRY	29B		X																452
	K-1 SLURRY	34B		X																453
	K-1 SLURRY	36A		X																454
	K-1 SLURRY	41B		X																455
6578	K-2 SLURRY	5		X		X					X	X	X	X	X	X	X	X	X	397
6579	K-2 SLURRY	9		X		X					X	X	X	X	X	X	X	X	X	398
6580	K-2 SLURRY	15		X		X					X	X	X	X	X	X	X	X	X	399
	K-2 SLURRY	19B		X		X					X	X	X	X	X	X	X	X	X	456
	K-2 SLURRY	24B		X		X					X	X	X	X	X	X	X	X	X	457
	K-2 SLURRY	29B		X		X					X	X	X	X	X	X	X	X	X	458
	K-2 SLURRY	34B		X		X					X	X	X	X	X	X	X	X	X	459
	K-2 SLURRY	36A		X		X					X	X	X	X	X	X	X	X	X	460
	FEED(START-UP)OIL	24B		X																436
	FEED(START-UP)OIL	29B		X																437
	FEED(START-UP)OIL	34B		X																438
	FEED(START-UP)OIL	36A		X																439
	FEED(START-UP)OIL	41B		X																440
6557	ASOH	5		X	X															386
6558	ASOH	8		X	X															387
6559	ASOH	9		X	X															388
6560	ASOH	15		X	X															389
6561	ASOH	17		X	X															390
	ASOH	19B		X	X															479
	ASOH	24B		X	X															480
	ASOH	29B		X	X															481
	ASOH	34B		X	X															482
	ASOH	36A		X	X															483
6562	SOH	5	1	X	X															381
6563	SOH	8	1	X	X															382
6564	SOH	9	1	X	X															383
6565	SOH	15	1	X	X															384
6566	SOH	17	1	X	X															385
	SOH	19B	1	X	X															475
	SOH	24B	1	X	X															474
	SOH	29B	1	X	X															475
	SOH	34B	1	X	X															476
	SOH	36A	1	X	X															477
	SOH	41B	1	X	X															478
6572	PFL	5		X	X	X					X	X	X	X	X	X	X	X	X	391
6573	PFL	9		X	X	X					X	X	X	X	X	X	X	X	X	392
6574	VSOH	15		X	X	X														393
	PFL-VSOH	19B		X	X	X														461
	VSOH	24B		X	X	X														462
	VSOH	29B		X	X	X														463
	VSOH	34B		X	X	X														464
	PFL	36A	2	X	X	X					X	X	X	X	X	X	X	X	X	465
	PFL	41B	2	X	X	X					X	X	X	X	X	X	X	X	X	466
6575	PFC	5	2	X			X	X	X	X										394
6576	PFC	9	2	X			X	X	X	X										395
6577	VSB	15	2	X			X	X	X	X										396
	VSB	19B	2	X			X	X	X	X										444
	VSB	24B	2	X			X	X	X	X										445
	VSB	29B	2	X			X	X	X	X										446
	VSB	34B	2	X			X	X	X	X										447
	PFC	36A	2	X			X	X	X	X										448
	PFC	41B	2	X			X	X	X	X										449
6559	CAS BTMS	5	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	379
6560	CAS BTMS	9	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	380
6561	CAS BTMS	15	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	381
	CAS BTMS	19B	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	486
	CAS BTMS	24B	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	487
	CAS BTMS	29B	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	488
	CAS BTMS	34B	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	489
	CAS BTMS	36A	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	490
	CAS BTMS	41B	2	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	491
6581	FEED COAL HRI/HTI #6213		3, 4																	400
	HDPE FEED		3, 4																	
	PP FEED		3																	
	PS FEED		3, 4																	
6582	MAKE-UP OIL L-814			X			X	X	X	X										401

LEGEND
A = SPECIAL ANALYSES, SEE KEY
B = WHOLE SAMPLE: ^{1}H-NMR
C = WHOLE SAMPLE:PHENOLIC -OH
D = WHOLE SAMPLE:MICROAUTOCLAVE TEST
E = WHOLE SAMPLE:THF EXTRACTION
F = THF-INSOLS OF WHOLE SAMPLE:ASH
G = THF-SOLS OF WHOLE SAMPLE:PHENOLIC -OH
H = THF-SOLS OF WHOLE SAMPLE:SOLVENT FRACTION. (O,A,P)
I = WHOLE SAMPLE:650°F DISTILLATION

▒ - DONE
J = 650°F- DISTILLATE: ^{1}H-NMR
K = 650°F- DISTILLATE:PHENOLIC -OH
L = 650°F- DISTILLATE:MICROAUTOCLAVE TEST
M = 650°F+ RESID:THF EXTRACTION
N = THF-INSOLS OF 650°F+ RESID:ASH
O = 650°F+ RESID: ^{1}H-NMR
P = THF-SOLS OF 650°F+ RESID:PHENOLIC -OH
Q = THF-SOLS OF 650°F+ RESID:SOLVENT FRACTION. (O,A,P)

KEY TO SPECIAL ANALYSES 1 = GC/MS; 2 = INSPECT FOR HDPE; 3 = ULT., PROX., CI, BTU, ASH ELEMENTS, S FORMS (OXIDATION INDEX); 4 = ULT., ASH FROM POC-2

APPENDIX 2

CMSL-10 SAMPLE REQUEST

CONSOL Inc.
Research & Development
4000 Brownsville Road
Library, PA 15129-9566
412-854-6600
FAX: 412-854-6613
412-854-6748

June 8, 1995

Dr. V. Pradhan
Hydrocarbon Technologies, Inc.
P. O. Box 6047
New York and Puritan Avenues
Lawrenceville, NJ 08648

Dear Vivek:

Our sample request for Run CMSL-10 is described below. We are requesting material in sufficient quantities to allow for sample distribution to other research groups, as needed. We understand that you cannot always provide the requested amounts, and we can work with smaller quantities.

We would like to receive from each CMSL-10 run condition: (1) 250 g of separator overhead (SOH) and 250 g of atmospheric still overhead (ASOH) or 250 g of SOH/ASOH blended in the correct product ratio; (2) 350 g of pressure-filter liquid (PFL); (3) 350 g of pressure-filter cake (PFC); (4) 350 g of continuous atmospheric still (CAS) bottoms; (5) 350 g of interstage sample (first-stage product); and (6) 250 g of feed slurry. Please also include: (7) 350 g of the start-up/make-up oil; (8) 250 g samples of SOH and ASOH liquids from any bypass periods of the in-line hydrotreater; and (9) a fresh 300 g sample of the feed coal.

We have not yet received the three interstage samples we were expecting from Run CMSL-8. Also, we are still interested in similar sample sets you may have from Runs CMSL-6 and CMSL-7, even though the sample quantities may be limited. We would appreciate any of these samples that you can provide.

Let us know of any problem areas with this request. Thank you for your assistance.

Sincerely,

Gary

G. A. Robbins
Sr. Research Chemist

/ls

cc: A. G. Comolli - HTI
M. A. Nowak - PETC
E. B. Klunder - PETC
F. P. Burke
R. A. Winschel
S. D. Brandes

APPENDIX 3

UNIVERSITY OF DELAWARE QUARTERLY REPORT

THE KINETICS OF COAL LIQUEFACTION DISTILLATION RESID CONVERSION

QUARTERLY REPORT

4/16/95 - 7/15/95

Michael T. Klein
Principal Investigator

William H. Calkins
Co-Principal Investigator

He Huang
Research Associate

and

Shaojie Wang
Visiting Scientist

Center for Catalytic Science and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19716

Date Published
July 18, 1995

Subcontract from CONSOL under DOE Contract DE-AC22-94PC93054

EXECUTIVE SUMMARY

Analytical methods have been worked out and. are being used to measure the conversion of coal derived vacuum resid to material boiling below 850 °C when the conversior. system uses small amounts of sulfided molybdenum naphthenate catalyst. When large amounts of Ni/Mo on alumina catalyst are used, we have yet to settle on a suitable method for determining conversion to low boiling materials. This problem is now being addressed.

A gas chromatograph has been received which will be used to determine the off-gas composition from the reactor and the number of volatile components evolved from the TG SYMDIS method.

A Netzsch thermogravimetric analyzer has been received which will be connected by a temperature controlled transfer line into a high resolution mass spectrometer for investigating the composition of coal derived vacuum resids and their hydropyrolysis products. More work must be done on the instrument to eliminate excessive noise which would interfere with the interpretation of the results.

Modelling work on the coal derived vacuum resids is getting started. Further progress will depend on obtaining TG SYMDIS data and Sara fractions for molecular weight determination, necessary steps in the modelling computations.

QUARTERLY REPORT

ANALYTICAL DEVELOPMENT

A Hewlett-Packard Model 5710A Gas Chromatograph has been received from CONSOL. When outfitted with a GC column and suitable inlet connections, this instrument will be used to follow the composition of the off gas from the conversion reactor as well as the volatile products from the TG SYMDIS analysis of the resid conversion products.

A Netzsch Thermogravimetric Analyzer together with a special temperature controlled transfer line has now been received. We plan to use it in conjunction with a high resolution mass spectrometer in the Chemistry Department to investigate the composition of the resid hydroconversion products in order to obtain information about the chemical composition of these materials and how they vary from resid to resid. Thus far, the instrument has not been sufficiently noise free that it can be used for this purpose. We are working with the vender to get the instrument sufficiently stable so that it can be coupled with the mass spectrometer.

RESID CONVERSION KINETICS

Table 1 shows a compilation of a number of resid hydroconversion runs together with the ash content of the residues as determined by TGA. As shown in the table, all the runs shown are either uncatalyzed or catalyzed with about 0.9 wt% molybdenum as sulfided molybdenum naphthenate. In these cases, the added catalyst contributes only a minor amount to the total ash formed (the basis for calculation of the conversion to soluble products). A number of runs have also been made using Ni/Mo on alumina catalyst in an amount equivalent to the resid used. All these runs were summarized in the last quarterly report. However, these experiments are not included in Table 1 since a satisfactory method of determining the resid ash in the presence of the large amount of alumina supported catalyst has not yet been worked out.

It should also be pointed out that we are interested in % conversion to material boiling below 850°F. This depends on the % solubilized and the TGA SYMDIS method developed previously. These measurements are being determined but have not yet been completed.

MODELLING THE RESID UPGRADING PROCESS

Background

The time-honored modeling technique for heavy ends upgrading uses lumped kinetics schemes, where molecular components are grouped by boiling points or solubility classes (e.g. resin or asphaltene). However, these lumps tend to have little chemical significance

and the effects of the reaction environment are usually ignored. They also provide little information about liquid or solid product quality.

The approach developed by Neurock et al. (1), stochastically builds a sample of representative molecules which can react along known reaction pathways. The heart of the model is the construction of the resid molecules by a Monte Carlo sampling technique. Any molecule can be thought of as a juxtaposition of molecular attributes (e.g. number of aromatic rings, number of side chains, etc.). The likelihood that an attribute has a particular value is given by a probability density function (PDF). The shape of these PDF's are characteristic for a resid. By systematic Monte Carlo sampling of these PDF's, representative molecules are built. A construction flow chart (2) is shown in Figure 1. Figure 2 demonstrates the Monte Carlo construction of a naphthenic molecule (2).

Ensuring that the PDF's are correct for a given resid is also of critical importance. Trauth et al. (2), established a technique which optimizes the PDF's for a given resid. Because the gamma distribution has: 1). semi-theoretical significance (3); 2). empirical credibility derived from numerous experimental observations; and 3). the mathematical flexibility to describe distributions of attributes for resids accurately, it was used as the PDF form for the Monte Carlo simulation. The quantitative parameters of these gamma distribution functions are optimized by comparing properties (e.g. SIMDIS weight fractions, H/C ratio, etc.) of the Monte Carlo representation against experimental measurements, using the Global Simulated Annealing algorithm.

Current Work

Recently the construction and reaction algorithms have been updated to reduce CPU demand(4). Sulfur has also been incorporated into the most recent models. The reaction algorithm is currently being adjusted to account for the incorporation of sulfur. Inclusion of other heteroatoms will be based on the sulfur work. Types and reactivities of nitrogen and oxygen moieties will need to be determined for this work. One note of importance is that most of the development of the Monte Carlo work to date has been for petroleum resid. The differences between petroleum resid and coal resid may require some modifications.

Currently, most of the necessary analytical information for the CONSOL resids has been provided. Elemental analysis, resid molecular weights using FIMS, and proton NMR data have been provided. Dr. Calkins and Dr. Huang are currently running SIMDIS on the complete resids using a modified TGA. As soon as the various SARA fractions arrive, VPO molecular weights will be determined for each of the various weight fractions. These are the essential analytical information necessary for petroleum resid.

Dichlorobenzene was experimentally found to give the best undissociated molecular weight for petroleum resids and their SARA fractions. Determination of molecular weights for the naphthenic, aromatic, and resin fractions should be relatively simple since each of these fractions should readily dissolve in dichlorobenzene. Due to the nature of coal resid

asphaltenes, dichlorobenzene may not be sufficient to dissolve the complete sample. Some experimentation may be necessary to determine a suitable solvent which can break up the acid-base interactions common in coal resid asphaltenes.

Once the SIMDIS fractions and the SARA fraction molecular weights have been determined, the PDF parameters will be optimized for each feed. Optimization of the PDF parameters for a given feed will take a few days for each resid. Construction and batch reaction of a given feed should take only a couple of minutes once the PDF parameters have been optimized.

LITERATURE CITED

1. Neurock, M.,Libanati, C., Nigam, A., and Klein, M. T., *Chem. Eng. Sci.*, 45, 2083 (1990).

2. Trauth, D. M., Stark, S. M., Petti, T. F., Yasar, M., and Klein, M. T., *PREPRINTS, Div. Petrol. and Fuel Chem., ACS* (1993).

3. Flory, P.J., *J. Am. Chem. Soc.*, 58, 1877 (1936).

4. Campbell, D. M., Klein, M. T., *PREPRINTS, Div. Petrol. and Fuel Chem., ACS* (1995).

Table 1 STBR Reactor Runs and Analytical Results

Sample	C001	C004	C006	C007	C008	C009	C014	C015	C017	C018
T(C)	19	410	411	408	406	408	392	403	409	408
t(min)	15	7	15	15	15	15	15	15	0.06	1
Catalyst (Mo, wt%)*					0.9	0.9	0.9	0.9	0.9	0.9
SA (g)**			1	1	1	1			1	1
Gas	H2	N2	H2	N2	N2	H2	N2	H2	H2	H2
Elemental Analysis										
C	58.71	53.27	51.22	53.08	55.55	46.94	52.82	49.43	53.15	49.73
H	2.76	2.33	2.24	2.24	2.43	2.16	2.46	2.29	2.59	2.30
N	1.08	1.01	0.99	1.04	0.91	0.85	0.84	0.86	0.94	0.85
S	3.21	3.57	3.92	3.82	4.49	5.77	3.79	3.82	3.58	5.44
Ash	39.27	42.71	44.97	43.50	40.13	49.50	43.78	46.68	42.20	45.93
O (by difference)	-5.03	-2.89	-3.34	-3.68	-3.51	-5.34	-3.69	-3.23	-2.46	-4.35
Selected Ash Composition										
MoO3	0.09	0.02	0.01	0.02	7.71	7.39	3.27	7.38	4.51	6.77
Al2O3	13.18	13.07	12.82	12.66	11.65	11.48	13.09	11.82	12.31	11.86
SiO2	24.70	24.17	24.24	24.29	21.93	21.55	24.48	21.88	23.00	21.98
Ash (by TGA)	35.69	42.11	43.27	40.70	37.40	45.39	42.58	45.95		

* Molybdenum naphthenate

** SA Sulfiding agent: (CH3)2S2

Table 1 (Continued)

Sample	C019	C020	C021	C022	C024
T(C)	412	410	411	408	408
t(min)	3	5	10	30	60
Catalyst (wt%)*	0.9	0.9	0.9	0.9	0.9
SA (g)**	1	1	1	1	1
Gas	H2	H2	H2	H2	H2
Elemental Analysis					
C	51.64	49.43	51.96	47.53	42.68
H	2.41	2.18	2.18	1.94	1.81
N	0.84	0.81	0.89	0.90	0.67
S	5.19	5.44	5.13	5.42	6.19
Ash	44.47	47.24	45.12	49.94	54.34
O(by difference)	-4.55	-5.22	-5.28	-5.75	-5.84
elected Ash Composition					
MoO3	6.96	7.07	6.54	6.51	7.00
Al2O3	11.61	11.36	11.26	11.60	11.86
SiO2	21.74	21.53	20.95	21.02	21.56
Ash (by TGA)					

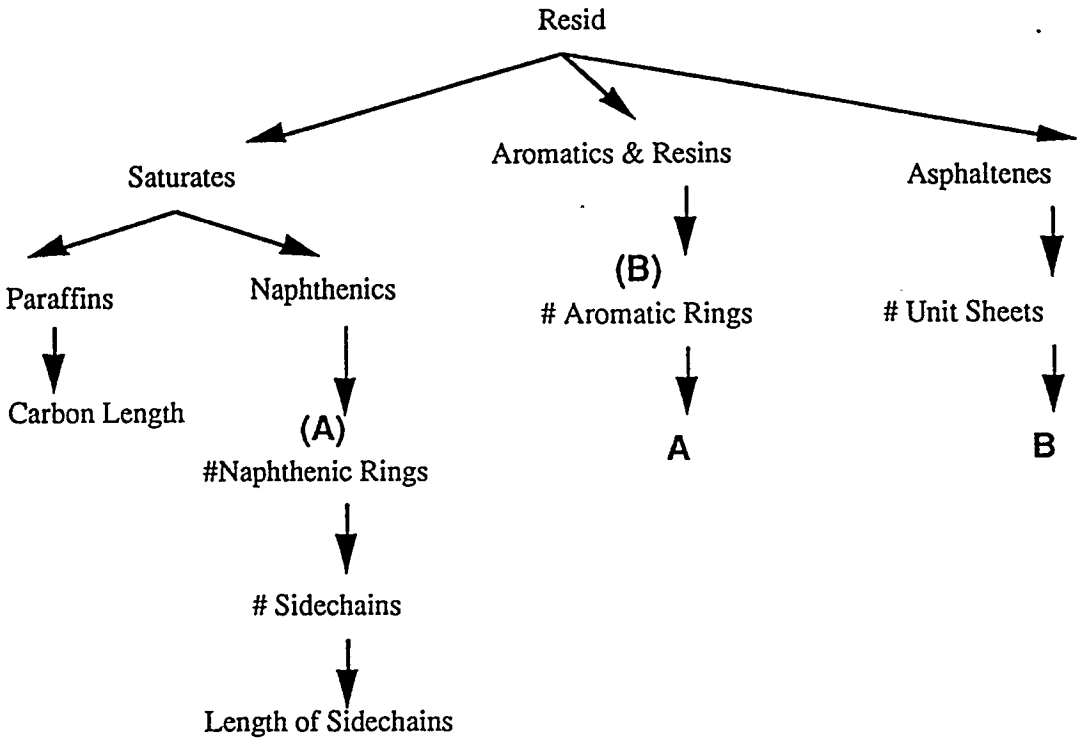


Figure 1: Resid construction technique based on sampling irreducible structural units

Cumulative Probability Distribution

Resultant Structure

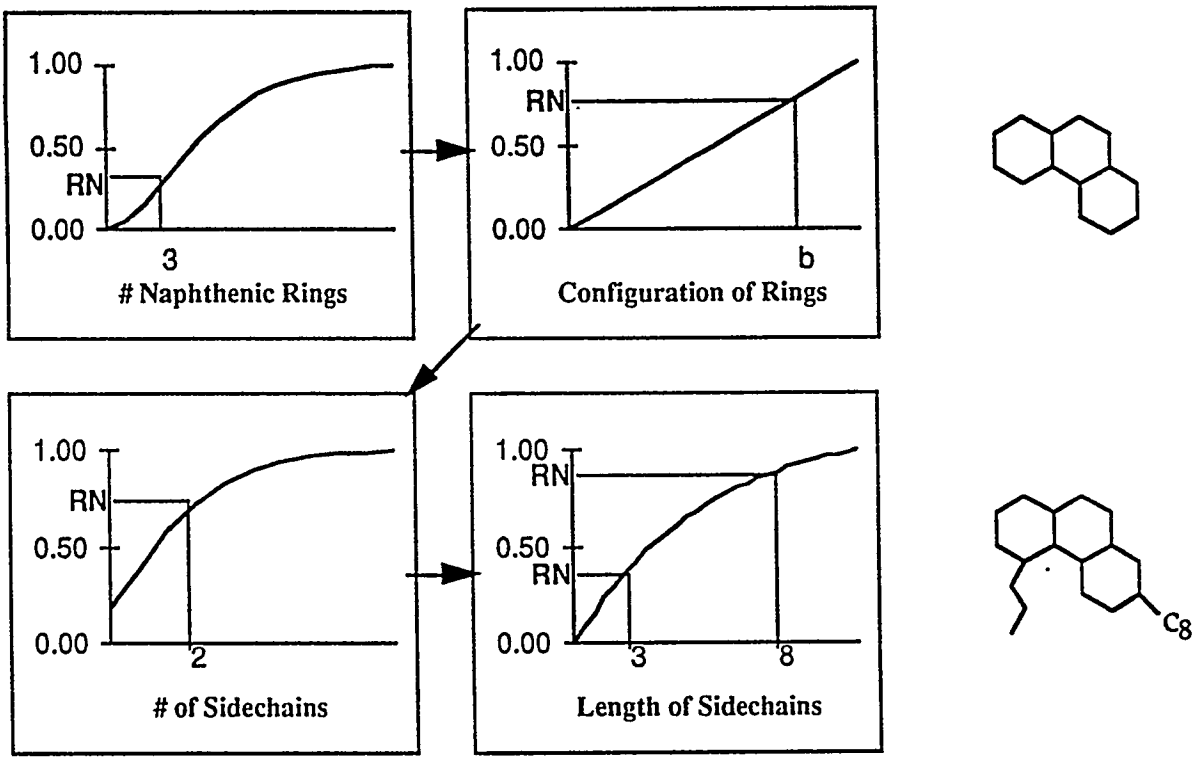


Figure 2. Stochastic construction of a resid molecule: pdf's are sampled to determine the value for each structural attribute.

APPENDIX 4

UNIVERSITY OF DELAWARE CONFERENCE CALL RECORD

RECORD OF CONFERENCE CALL

April 26, 1995

Re: University of Delaware Subcontract from CONSOL Under DOE Contract DE-AC22-94PC93054

Participants: University of Delaware
M. T. Klein
W. H. Calkins
D. Campbell
H. Huang

CONSOL
F. P. Burke
R. A. Winschel
S. D. Brandes

The main topic of this discussion was Delaware's requirements for analytical data to support the kinetic modeling work. A brief discussion followed on Delaware's 'isotrack' thermogravimetric analysis (TGA) method.

Mike Klein defined four categories of analytical needs for the modeling work. These are: 1. necessary or essential information; 2. highly desirable information; 3. desirable information; and 4. extraneous information. Information obtained in Categories 2 and 3 will provide improvements to the model constructed from information provided under Category 1. The analyses that were requested and the category in which they fall are listed below. Responsibility for which research group (CONSOL or Delaware) will perform the analyses also is noted. Analyses that will be performed by organizations other than CONSOL or Delaware are identified. Arrangements for analyses by third parties will be made by CONSOL. All 15 feed materials will be analyzed by at least Categories 1 and 2 methods. Selected reaction products also will be analyzed.

Analysis of Feed Materials

Category 1:

- ^{1}H-NMR CONSOL's standard method of dividing the spectra into 7 groups is acceptable to Delaware. (CONSOL)
- elemental analyses: C, H, N, S(total), O(by difference), ash (CONSOL)
- chromatographic separation: a SARA (saturates, aromatics, resins, asphaltenes) separation is considered sufficient by Delaware, however, a

separation into more (defined) classes can only add to the information content of the model. A separation scheme such as SESC (sequential elution solvent chromatography), which produces 9 fractions was offered as an example of such a separation. (CONSOL)

- molecular weight determination of chromatographic fractions: VPO (Delaware)
- distillation: TGA Isotrack method (Delaware) or SimDist method (Delaware)

Category 2:

- ^{13}C-NMR: Structural parameters (12) and molecular descriptors (8) via the techniques devised by R. Pugmire (University of Utah) are considered to be very helpful (WRI)
- phenolic -OH content (CONSOL)

Category 3:

- Field ionization mass spectrometry (FIMS) on a few carefully selected samplesfor molecular weight profiles of feeds and STBR products (SRI)

Category 4:

- This category consists of information that has no application in the model. Examples of Category 4 data are viscosity and Conradson carbon number. The usefulness of ESR data and whether or not it is a Category 4 analysis will be examined by Delaware.

Analysis of reaction products is not considered essential.

- All methods listed in Category 1 for the feed materials are, therefore, Category 2 analyses when applied to the selected reaction products. Similarly, methods listed in Categories 2 and 3 for the feed materials are of even lower priority for the selected reaction products.

Mike asked that the experimental error (standard deviation) on all analytical measurements be provided.

The information that Mike's group will directly obtain from Bill's work to produce the model are: 1. yield (or conversion) values, 2. experimental variables, and 3. the data from the TGA isotrack method on the feedstocks that will be used, when possible, in lieu of distillation.

CONSOL's planned work in shaker-bomb microreactors was briefly discussed. Mike feels that data provided in a reactor system different than the short contact time batch reactor (SCTBR) would be helpful in providing data for checking the validity of the model. Bill suggested that one advantage of the CONSOL work may be that longer residence times (greater than 60 min) can be achieved. Higher pressure operation also is possible.

In a brief discussion of the TGA isotrack method, He Huang clarified some issues raised in the recent quarterly technical report submitted by Delaware. The run temperature of 280 °C was chosen so that both the lowest boiling material and the material boiling close to 850 °F can evolve from the TGA in a reasonable time (20 - 30 min). The longer run times reported in the quarterly report were used to produce boiling point distribution curves of samples with a wide boiling point range. Using higher temperatures seems to result in loss of accuracy in the boiling point curve. Runs have been made under vacuum (about 35 mm Hg). In a vacuum, however, it is not possible to achieve the rapid heating obtained in the atmospheric pressure system because of the configuration of the pan in the quartz chamber and the furnace. In the atmospheric pressure system, the pan is inserted into a preheated quartz chamber which is already in place in the furnace. In the vacuum system, the quartz tube and sample must be in place to pull a vacuum; this prevents preheating. When the assembly is inserted in the furnace, there is a much slower heat up that is exacerbated by the low heat conduction to the sample, the pan, and the thermocouple in vacuum.

APPENDIX 5

PAPER FOR 210TH NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

CAUSTIC WASHING FOR REFINING OF DIRECT COAL LIQUEFACTION PRODUCTS

R. A. Winschel
P.-Z. Zhou*
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Prepared for Presentation at the
210th National Meeting of the American Chemical Society

Chicago, IL
August 20-25, 1995

CAUSTIC WASHING FOR REFINING OF DIRECT COAL LIQUEFACTION PRODUCTS

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KEYWORDS: Liquefaction, Refining, Phenols

INTRODUCTION

Extensive research and development sponsored by the U.S. DOE/PETC over the past two decades has resulted in dramatic improvements in the quality of direct coal liquefaction products. High-quality coal-derived distillates are obtainable from catalytic two-stage liquefaction (TSL) processes, such as those developed at the Wilsonville, AL pilot plant and the Hydrocarbon Technologies Inc. (HTI) pilot plant and bench units. The products of the Wilsonville and HTI TSL operations are suitable as high quality feedstocks for producing transportation fuels in a refinery. These products have important quality advantages over crude petroleum: they are distillates boiling below about 700°F and are thus virtually free of resid and metals, and they have very low sulfur contents and low nitrogen contents.[1-3] The coal liquids have carbon and hydrogen contents and Watson characterization factors within the range of crude petroleums.[1-3] However, relative to crude petroleum, the crude coal products have elevated oxygen contents[(1-3)]. Although these oxygenated species are found at elevated concentrations throughout the boiling range of the coal liquids, they are most frequently concentrated in the heavy naphtha and light kerosene fractions. For example, when the oxygen content of coal liquids is plotted as a function of boiling point, there is often a maximum in the curve between 355 °F and 465 °F (Figure 1 and References 1, 2, and 4).

Phenolic compounds are the predominant oxygen-containing components in the coal liquids;[4] the curve maximum represents phenols with zero to three alkyl carbon substituents. Phenolic compounds must be reduced to low concentrations to produce finished transportation fuels. In a typical modern petroleum refining scheme, this would be accomplished by hydrotreating. However, because coal liquids have high concentrations of phenolics, it may be advantageous to reduce their concentration prior to hydrotreating by some other route, for example, by caustic extraction. Although caustic washing could not replace hydrotreating to produce finished fuels from the oils described here, this route for pre-removal of phenols could have several advantages over hydrotreating the phenolic containing oils: it would reduce the overall hydrogen demand, it could produce a valuable by-product (cresylic acid), and it would simultaneously strip from the oil mercaptans and hydrogen sulfide in addition to the phenolics. Indeed, caustic washing was once a common unit operation in petroleum refineries because of its ability to sweeten light distillates.[5] The cresylic acid could be sold as a by-product or perhaps methylated to produce methyl aryl ethers,[6] which could be used as a high octane oxygenate gasoline extender. Presented here are results of experiments conducted to recover a cresylic acid by-product from crude coal liquids, while simultaneously improving the quality of the liquid. The quality improvement in the coal liquid and the characterization of the by-product cresylics are discussed.

EXPERIMENTAL

The net products of three liquefaction runs that represent variations of state-of-the-art technology were characterized in detail. The three samples were generated at the Wilsonville 6 ton/day pilot plant (Run 260D) and the HTI 2 lb/hr bench unit (Runs CC-15 and CMSL-2), as described in Table 1. The characterization scheme included fractional distillation and analysis and inspection of the fractions. Some of the distillation fractions were caustic washed to remove phenolics and the recovered raffinate and caustic extract fractions were also characterized. The exact caustic washing procedure used varied among the samples; however, the general scheme was to contact the oil in a separatory funnel multiple times with NaOH (either 20 wt % or 6 wt % solutions) then with water, to acidify the extract with concentrated aqueous HCl, then to extract the phenols with methylene chloride and to remove the methylene chloride by rotary evaporation. Raffinate and caustic extract yields are determined gravimetrically. Some losses resulted from evaporation and handling during the extraction scheme. The complete backgrounds of the samples, details of all experimental methods and characterization data appear in the original reports of this work.[7-9] Phenolic -OH concentrations were determined by Fourier-transform infrared spectroscopy.[10] The caustic extracts also were characterized by gas chromatography/mass spectrometry (GC/MS) with a HP 5970 system equipped with a 30 m x 0.25 mm DB-5 column (0.25 μm film thickness) as follows: 20 psig He carrier gas; splitless injection as 1% solutions in THF; injection port at 300 °C; column temperature program - 5 min at 35 °C, to 100 °C at 35 °C/min, to 320 °C at 4 °C/min; scan from 45 to 300 amu; spectra searched against the Wiley/NBS mass spectral library; identifications based on search results and supplemented by

retention times; normalized quantitation is based on peak area divided by total peak area of all phenolics found.

DISCUSSION

The oxygen contents, determined by difference, of the distillation fractions of the three crude coal liquids are plotted in Figure 1 as a function of the mid boiling point of the fraction. Two of the three curves show maxima between 355 and 465 °F. Material in this boiling range tends to have relatively high concentrations of phenolic compounds. For example, Table 2 shows that the 380-510 °F fraction has the highest phenolic -OH concentration of the four distillation fractions of the Wilsonville Run 260D sample.

The fractions of the Wilsonville Run 260D sample that were caustic washed include the naphtha (IBP-380 °F), jet or kerosene (380-510 °F), diesel fuel (510-650 °F), and residuum (650 °F+) fractions. Table 2 shows the yields of raffinate and extract from each extraction and the phenolic -OH concentration in each fraction. The phenolic -OH concentrations (Table 2) of the raffinates show that caustic washing was quite effective at removing phenolics from the fractions boiling below 510 °F. In fact, for these raffinates, phenolic -OH was near or below detection limits. Caustic washing was not very effective for the higher boiling fractions. Not only was caustic washing less effective for the higher boiling fractions, it was also less selective; GC/MS analyses showed that the caustic extracts of the higher boiling fractions were contaminated with hydrocarbons. For this reason, and because the highest concentration of phenolics tend to exist in fractions that boil between 355 and 465 °F (Figure 1 and References 1, 2, and 4), only the naphtha (IBP-380 °F) and kerosene (380-510 °F) fractions of the HTI Run CC-15 sample and the "swing cut" (350-400 °F) fraction of the HTI Run CMSL-2 sample were caustic washed. The raffinates of the fractions from HTI Runs CC-15 and CMSL-2 were characterized by the same set of inspection tests as the original, unextracted fractions. The caustic extracts of the fractions from all three runs were characterized by GC/MS analysis and phenolic -OH determination.

The caustic extract yields range from 1.1 to 4.6% and losses (100% - yield of raffinate - yield of extract) range from 0.1 to 4.7%. The variations result from the different properties of the fractions, and perhaps from the use of different caustic washing procedures.

Table 3 compares the inspection data of the raffinates with the corresponding data of original, unextracted fractions. For the IBP-380 °F fraction of Run CC-15, the lower Reid vapor pressure of the raffinate appears to result from the loss of light material during the caustic wash. Properties of that fraction that showed improvement from caustic washing include acidity, copper strip corrosion, existent gum, bromine number, basic nitrogen, oxidation stability, heat of combustion, and mercaptan sulfur. The quality of the fraction in terms of its suitability as gasoline are somewhat improved relative to the unextracted fraction. The major improvements in the 380-510 °F fraction of Run CC-15 from caustic washing include acidity and mercaptan sulfur. Other improvements include oxygen (by diff.), viscosity and bromine number.

For the 350-400 °F fraction of HTI Run CMSL-2, the property which showed the greatest improvement from caustic washing is the mercaptan sulfur content. Many other properties (e.g., bromine number, acidity, oxygen by diff.) show some changes that indicate the raffinate is a better stock for production of transportation fuels. The oxidation stability decreased; this may result from the removal of hindered phenols, which are known to act as antioxidants. However, the opposite effect was seen with the IBP-380 °F fraction of HTI Run CC-15, as discussed above.

The major components of the caustic extracts, as determined by GC/MS analysis, are provided in Table 4. Although the extracts of the higher boiling fractions contained some hydrocarbons, each caustic extract consisted primarily of phenolics. The high measured phenolic -OH concentrations of the caustic extracts (Table 2) confirm this. Depending on the boiling point of the fraction extracted, the caustic extracts consist of phenols with zero to four alkyl substituents.

SUMMARY

Caustic washing was found to be highly efficient and highly selective for the extraction of phenolics from the light distillate fractions (b.pt. <510 °F) of the products of modern two-stage direct coal liquefaction products. The extracts were composed almost entirely of phenolics and the lower boiling raffinates were almost devoid of phenolics. The properties of the raffinates as feedstocks or blendstocks for transportation fuels were moderately improved relative to the unextracted materials. Notable improvements included reduced acidity, mercaptan sulfur, oxygen (by diff.) and copper corrosion; other minor improvements also were seen. The composition of the caustic extracts (cresylic acids) depends on the boiling point of the material extracted, but primarily consists of phenols with zero to four alkyl substituents.

ACKNOWLEDGEMENT
This work was supported by the U.S. Department of Energy under contracts DE-AC22-89PC89883, DE-AC22-89PC88400, and DE-AC22-94PC93054. The inspection data and caustic washing of the HTI samples were performed by G. Sturm, J. Kim and J. Shay of the National Institute for Petroleum and Energy Research.

REFERENCES

1. Zhou, P.-Z.; Winschel, R. A.; Klunder, E. B., *Am. Chem. Soc. Div. Fuel Chem. Prepr.* 1994, *39*(4), 1205-1209.
2. Zhou, P.-Z.; Rao, S. N. "Assessment of Coal Liquids as Refinery Feedstocks", DOE Contract No. DE-AC22-89PC88400, February 1992.
3. Zhou, P.-Z. "Characterization of Direct Liquefaction Distillate Products", DOE Contract No. DE-AC22-89PC88400, 1994.
4. Zhou, P.-Z. "Recovery of Phenols From Coal Liquids", DOE Contract No. DE-AC22-89PC88400, March 1993.
5. Nelson, W. L., *Petroleum Refinery Engineering*, Fourth Ed.; McGraw-Hill: New York, 1958; Chapter 10.
6. Singerman, G. M. "Methyl Aryl Ethers from Coal Liquids as Gasoline Extenders and Octane Improvers", Report DOE/CE/50022-1, November 1980.
7. Kramer, R. L. in Report DOE/PC89883-34, November 1991.
8. Sturm, Jr., G. P.; Kim, J.; and Shay, J. in Report DOE/PC89883-92, January 1994.
9. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P., Reports DOE/PC89883-43, March 1992, DOE/PC89883-86, March 1994, and DOE/PC 93054-4, October 1994.
10. Burke, F. P.; Winschel, R. A.; Robbins, G. A., Report DOE/PC30027-61, March 1985.

TABLE 1. SOURCE DATA OF COAL LIQUID SAMPLES

Plant/Run	Feed Coal Seam	Process Description		
		Operating Mode	Catalyst	Reactor Temps., °F
Wilsonville 260D	Wyodak and Anderson	Catalytic/Thermal	Shell 324/Fe_2O_3	790/774
HTI CC-15	Wyodak and Anderson	Thermal/Catalytic	Fe_2O_3/Shell 317	800/775
HTI CMSL-2	Illinois No. 6	Catalytic/Catalytic	Shell 317/Shell 317	752-777/795-811

TABLE 2. YIELDS AND PHENOLIC -OH CONCENTRATIONS OF FRACTIONS

Fraction	Yields, wt % of Feed Fraction		Phenolic -OH Concentration, meq/g Sample		
	Raffinate	Caustic Extract	Feed Oil	Raffinate	Caustic Extract
Wilsonville Run 260D					
IBP-380 °F	92.7	3.7	0.40	0.02(a)	-
380-510 °F	94.7	3.6	0.92	0.07(a)	-
510-650 °F	94.4	4.6	0.52	0.27	-
650 °F$^+$ - Trial 1	95.4	1.9	0.41	0.28	-
650 °F$^+$ - Trial 2	97.9	2.0	0.41	0.31	-
HTI Run CC-15					
IBP-380 °F	92.9	2.4	0.13(b)	(c)	8.90
380-510 °F	92.1	4.0	0.24(b)	(c)	7.49
HTI Run CMSL-2					
350-400 °F	95.4	1.1	(c)	(c)	5.02

(a) Quantitation is uncertain at these extremely low concentrations
(b) Amine signal probably contributing to reported phenolic -OH concentrations
(c) Amine observed, no phenolic -OH detected

TABLE 3. INSPECTIONS OF ORIGINAL AND RAFFIANTE FRACTIONS

Property	HTI Run CC-15				HTI Run CMSL-2	
	<380 °F		380-510 °F		350-400 °F	
	Original	Raffinate	Original	Raffinate	Original	Raffinate
Spec. Gravity @ 60 °F (D4502)	0.7798	0.7775	0.8899	0.8882	0.8492	0.8484
API Gravity (calculated)	50.0	50.5	27.5	27.8	35.1	35.3
Elemental Analysis, wt %						
Carbon (D5291)	85.93	86.12	87.12	87.75	86.78	86.86
Hydrogen (D5291)	13.96	13.77	11.77	11.68	12.72	13.08
Sulfur (D3120)	0.03	0.03	0.03	<0.01	0.01	0.01
Nitrogen (D4629)	0.09	0.07	0.33	0.33	0.03	0.02
Oxygen (by diff)	0.00	0.01	0.75	0.23	0.46	0.03
Basic Nitrogen (UOP269)	0.082	0.058	0.274	0.264	0.023	0.023
Mercaptan Sulfur (D3227), ppm	51.5	9.7	45.2	<0.1	19.0	6.0
Viscosity (D445), cSt						
@ 210 °F	-	-	-	-	0.6653	0.6741
@ -20 °C	-	-	10.80	9.665	4.683	4.359
Refractive Index (D1218), @ 20 °C	1.42882	1.42836	1.49196	1.49072	-	-
Freezing Point (D2386), °F	-	-	-12	-13	-99	-95
Cloud Point (D2500), °F	-	-	-	-	<-60	<-60
Pour Point (D97), °F	-	-	-	-	<-60	<-60
Reid Vapor Pressure (D5191), psi	2.54	2.09	<0.01	<0.01	0.02	<0.01
Flash Point (D56, D93), °C	-	-	83	82	50	57
Group Analy. (ASTM D5134 & HC22)						
Paraffins, vol %	38.0	34.7	9.6	9.1	7.5	8.0
Naphthenes, vol %	45.7	48.8	43.1	46.0	61.3	61.5
Aromatics, vol %	8.7	9.2	41.4	41.9	28.4	27.8
Olefins, vol %	4.6	4.2	5.8	3.0	2.8	2.5
Benzene (PIANO, mod D5134)	0.089	0.078	-	-	-	-
Naphthalenes (D1840), vol %	-	-	4.23	3.74	0.48	0.32
Bromine Number (D1159)	3.62	2.37	5.08	2.69	3.00	2.71
Aniline Point (D611), °F	103.8	106.0	71.5	75.2	-	-
Smoke Point (D1322), mm			10.9	11.6	15.6	15.4
Acidity (D3242), mg KOH/g	0.05	<0.01	0.04	0.01	0.01	<0.01
Copper Corrosion (D130)	3b(dark)	2d(mod)	1a(slight)	1a(slight)	1a(slight)	1a(slight)
Existent Gum (D381), mg/100 mL	11.2	9.0	-	-	6.4	6.2
Oxidation Stability (D525), min	105	1440	-	-	1440	720
Thermal Stability (JFTOT) (D3341)	-	-	Fail	Fail	-	-
Octane No., Motor Method (D2700)	60.7	58.1	-	-	-	-
Octane No., Rsrch Method (D2699)	61.6	60.2	-	-	-	-
Heat of Combustion (D2382, D240), Net Btu/lb	18,509	18,651	17,918	18,043	18,401	18,411
Luminometer Number (D1740)	-	-	-	-	27.3	27.0

TABLE 4. COMPOSITIONS OF CAUSTIC EXTRACTS

Component	GC/MS Intensity, as % of Total Phenolic Intensity (No. of Resolved Peaks in Parentheses)				
	Wilsonville Run 260D		HTI Run CC-15		HTI Run CMSL-2
	IBP-380 °F	380-510 °F	IBP-380 °F	380-510 °F	350-400 °F
phenol	24(1)	0.4(1)	13(1)	-	-
o-cresol	15(1)	1(1)	21(1)	-	1.5(1)
m/p-cresol	31(2)	4(1)	24(1)	0.4(1)	1.5(1)
dimethyl phenol	13(6)	14(6)	21(5)	13(6)	32(5)
ethyl phenols	16(2)	13(3)	17(2)	8(2)	10(2)
C_3-phenols	1(5)	31(12)	4(6)	51(12)	37(11)
C_4-phenols	-	16(10)	-	24(12)	17(9)
indanol	-	18(1)	-	4(1)	0.3(1)
dihydroxytoluene	-	1(1)	-	-	-
tetralinol	-	2(1)	-	-	-

Only traces of hydrocarbon contaminants found in IBP-380 °F extracts.
Some hydrocarbon contaminants found in others.

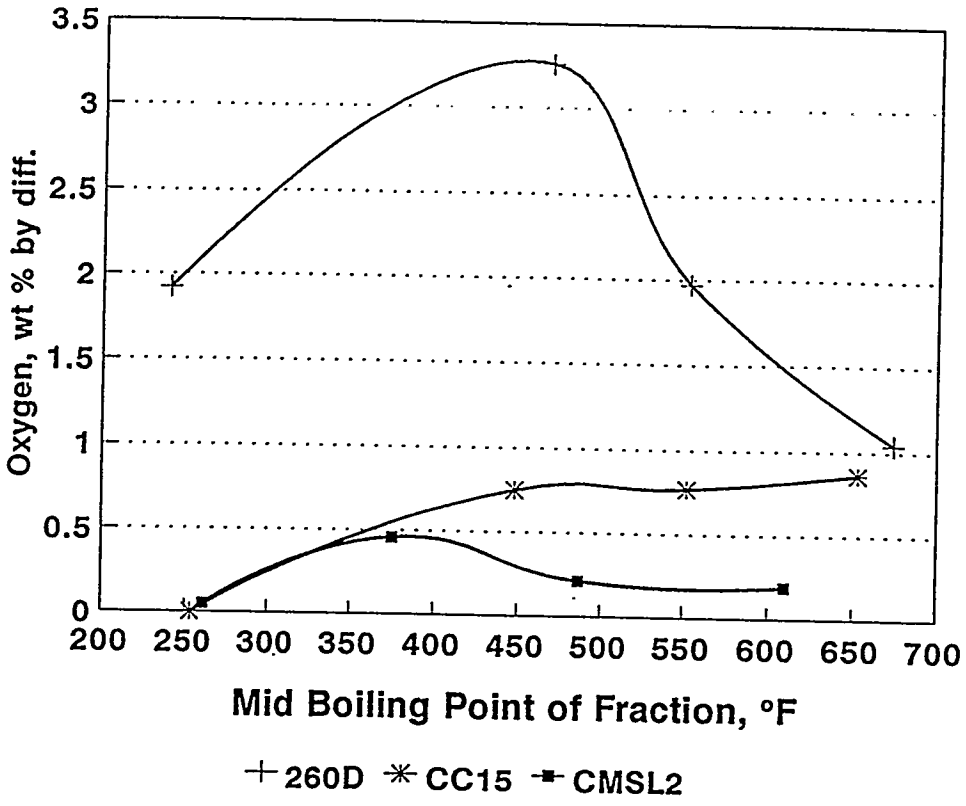

Figure 1. Oxygen Content (by diff.) versus Mid Boiling Point of Coal Liquid Fractions.

APPENDIX 6

PAPER FOR THE DOE LIQUEFACTION AND GAS CONVERSION
CONTRACTORS REVIEW CONFERENCE
August 29-31, 1995

TITLE: Characteristics of Process Oils from HTI Coal/Plastics Co-Liquefaction Runs

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INSTITUTION/ORGANIZATION: CONSOL Inc., Research and Development Department

CONTRACT NUMBER: DE-AC22-94PC93054

PERIOD OF PERFORMANCE: June 30, 1994 - June 30, 1997

OBJECTIVE:
The objective of this project is to provide timely analytical support to DOE's liquefaction development effort. Specific objectives of the work reported here are:

- to determine the fate of the plastics feedstocks, relative to coal-only operation;
- to determine the conversion of the feedstocks;
- to determine the product streams to which the feedstocks are converted (bottoms vs. distillate);
- to determine interactions of feedstocks;
- to determine how use of plastics feedstocks affect product quality; and
- to determine to what degree property differences reflect feedstock differences vs. other (process) condition changes, such as unit operations, space velocity, and catalyst age.

ACCOMPLISHMENTS AND CONCLUSIONS:
Introduction
During a few operating periods of Run POC-2, HTI co-liquefied mixed plastics with coal, and tire rubber with coal. Although steady-state operation was not achieved during these brief test periods, the results indicated that a liquefaction plant could operate with these waste materials as feedstocks. CONSOL analyzed 65 process stream samples from coal-only and coal/waste portions of the run. Some results obtained from characterization of samples from Run POC-2 coal/plastics operation are:[1,2]

1. Polystyrene (PS) products were identified and quantified in distillate product oil.

2. Incompletely converted high-density polyethylene (HDPE) was found as tetrahydrofuran (THF)-insoluble material in the ash-free-resid recycle stream. It was unclear to what extent this material was present in the ROSE bottoms stream. Unusual solubility behavior seems to be associated with HDPE-derived material in resid-containing streams. The broad implication is that HDPE was not completely converted in the liquefaction process.

3. The unusual presence of a product-oil sediment raised questions about the stability of the product oil.

5. Analytical issues were identified including how to identify and quantify HDPE, the appropriateness of coal liquefaction work-up procedures to

coal/plastics liquefaction, and how to measure the extent of plastics liquefaction.

Along with the analytical difficulties, the brevity of the coal/plastics liquefaction period in Run POC-2 prevented these issues from being resolved. To better evaluate these issues, Run CMSL-8 was performed at a smaller scale and over a longer period than Run POC-2. There were other differences too, such as reactor and temperature configuration and the feed coal used. However, the plant operated in solvent balance, which did not occur during the coal/plastics portion of Run POC-2. Solvent-balanced operation in Run CMSL-8 meant that samples, material balances, and performance results from Run CMSL-8 were representative of operation with the coal/plastics feedstocks. Coal/HDPE liquefaction was tested in Run CMSL-8, in addition to coal/mixed plastics liquefaction. The background and results from characterization of Run CMSL-8 process oil samples is presented below.

HTI Run CMSL-8 Background

A diagram of HTI's bench unit 227 as configured for Run CMSL-8 (also known as Run 227-85) is shown in Figure 1.[3] CONSOL analyzed feed samples, and samples from sample points 4 through 7, representing recycle and product streams. The operating conditions and process performance summary for the run are given in Table 1.[3] Operating performance was good early in the run, but as the run continued, the catalyst age increased, and the concentration of polyethylene in the feed was increased. The resid conversion decreased as the run progressed. Several adjustments were made to process conditions after period 16 to maintain performance and operability. Notable events were: the change from coal operation in period 6 to 75% coal and 25% mixed plastics prior to period 11; the increase in second-stage reactor temperature from 830 to 850 °F, an increase in first-stage space velocity from 30 to 40 lb dry feed/hr/ft^3 reactor prior to period 16; the increase in mixed plastics concentration to 33%, decrease in space velocity from 40 to 30 lb dry feed/hr/ft^3 reactor, and increase in dispersed Mo catalyst concentration from 100 to 200 ppm, prior to period 20; and, prior to period 22, the switch from 33% mixed plastics to 33% HDPE. Over the duration of the run, the supported catalyst reached an age of 966 lb dry feed/lb cat. Samples received as either period 22 or period 23 samples were considered to represent material balance period 22.

Analyses Performed

A brief description of the Run CMSL-8 samples and analyses conducted as CONSOL's baseline characterization is provided in Table 2. In this paper, the samples will be referred to by the abbreviations given in Table 2, e.g., SOH for the product oil, PFL for the recycle liquid, and PFC for the bottoms stream. The baseline analytical methods can be applied to many different kinds of samples, can be performed quickly, and have proven to be suitable for liquefaction process stream characterization. In addition to the routine laboratory analyses, non-routine characterization (such as FTIR characterization of certain samples) was performed, based on the Run POC-2 sample experience. Several samples were selected for specialized analyses, such as plasma desorption mass spectrometry (PDMS) and field ionization mass spectrometry (FIMS).

SOH Product Characteristics and Effects of On-line Hydrotreating

The separator overheads (SOHs) from periods 6 and 11 through 23 were consistently low in aromatic hydrogen and high in paraffinic hydrogen content (Figure 2). There was a small increase in paraffinic hydrogen from periods 16 to 20 to 23

coincident with increases in the HDPE concentration in the feed (8.75 to 11.5 to 33 wt % dry feed in those periods). There was no change in paraffinic hydrogen content from period 6 (coal-only) to period 11 (coal/mixed plastics). However, a substantially lower paraffinic hydrogen content was observed when the on-line hydrotreater was by-passed in period 9. This indicates that, because of extensive upgrading in the hydrotreater, the paraffinic hydrogen content of the SOH may be relatively insensitive to other process changes. The product oil (SOH) sample from period 9, in which the on-line hydrotreater was by-passed, is much poorer in quality than the SOHs produced with the hydrotreater in place. Differences included: medium brown in color vs. colorless, presence of a "coal liquid" odor, more aromatic, less paraffinic, and considerably higher phenolic -OH concentration (Figure 2). The effects of hydrotreating observed in this run were greater than those observed in Run POC-2.[1] This may be because the distillate hydrotreated in Run CMSL-8 is a thermal distillate, and the distillate of Run POC-2 came from a catalytic reactor.

Gas chromatography-mass spectrometry (GC-MS) total ion chromatograms of SOH samples (Figure 3) show that replacing a portion of the coal with mixed plastics (from period 6 to period 11) and the switch from mixed plastics to HDPE (from period 11 to period 22) increased the concentrations of n-paraffins in the SOHs, and shifted the n-paraffins to higher molecular weight. Thus, HDPE appears to be an important source of the n-paraffins in the SOHs produced after period 6. Two peaks corresponding to ethylbenzene and cumene (isopropylbenzene) are marked in Figure 3. These components are polystyrene (PS) liquefaction products. Cumene was not found in the coal-only period SOH, and ethylbenzene was present at about 1% concentration in the coal-only and coal/HDPE periods 6 and 23. ^{1}H-NMR results indicate that PS products persisted in the SOH product from the coal/HDPE period. In the NMR spectra of the SOHs, ethylbenzene features are nonexistent in the coal period SOH, quite prominent in the coal/mixed plastics period SOHs, and observable, but small, in the coal/HDPE period SOH.

The PS products were quantified by GC-MS and ^{1}H-NMR (Table 3). The area of the ethylbenzene and cumene peaks, as a percentage of the total ion chromatogram was used to estimate the concentration of these components in the SOHs. The alkylbenzene concentration of the SOHs was estimated (as ethylbenzene) by integration of the ^{1}H-NMR peak near 7.1 ppm. Based on these estimates, ethylbenzene and cumene constitute about 8-15 wt % of the coal/mixed plastic period SOHs (with the HTU in use), less than 1 wt % of the coal/HDPE period SOH, and about 2 wt % or less of the coal period SOH. When the hydrotreater was by-passed with the coal/mixed plastics feed, the concentration increased to about 15 to 23 wt % of the SOH. Approximately 50% of the PS fed to the process can be accounted for as these alkylbenzene products (with the hydrotreater operating).

HDPE in Recycle and Resid Samples

The PFLs from the coal/plastics periods 11, 16, 20, and 22 contained 15 to 30 wt % THF insolubles. These insolubles were tan with white specks early in the run and dark brown later in the run. The presence of THF insolubles in the PFL is a unique feature of coal/plastics processing. PFLs from coal-only operations (including period 6 of this run) typically contain little or no THF-insoluble material. The FTIR spectra of insolubles from coal/plastics periods 11 and 22 were similar and indicated that they are polyethylene-like material (Figure 4). PFL 850 °F$^+$ distillation bottoms from two of three coal/mixed-plastics periods separated into two solid phases upon cooling; none of the other PFL resids behaved in this way. The two phases differed in physical characteristics and

color. Diffuse reflectance FTIR (Figure 4) was used to examine both phases of one of the resids. The upper phase appeared to be predominantly plastic derived (much of it PE), and the lower phase is predominantly coal derived. The spectrum of the upper brown phase indicated primarily aliphatic hydrocarbons with PE-like features. Aromatic hydrocarbon peaks also were significant, but no features indicated the presence of heteroatomic functional groups. The spectrum of the lower black phase showed more intense aromatic hydrocarbon peaks than did the upper phase, and a significant amount of aliphatic hydrocarbon in the lower phase, but no distinctive PE-like features. The spectrum of the lower phase also contains prominent peaks from heteroatomic functionality, perhaps N-H and O-H.

Samples of both PFL resid phases, along with other samples from Run CMSL-8, also were characterized by field-ionization mass spectrometry (FIMS) at SRI International.[4-6] The pyrolysis profiles are shown in Figures 5a-b and the FIMS spectra in Figures 5c-h. Volatilization of each sample was nearly complete. The pyrolysis profiles show that HDPE pyrolyses to low molecular weight components at about 430 °C (Figure 5a), and that the THF-insoluble sample from the period 22 PFL is nearly all HDPE (Figure 5b). In the mass spectra, the HDPE pyrolysis products are lower in molecular weight and generally distinct from the coal-derived resid components (Figure 5c-h). These spectra also confirm the identification of the period 22 PFL THF insolubles as nearly pure HDPE (Figure 5c-d), and show that HDPE is present to varying degrees in the other samples from coal/plastic operating periods (Figure 5c-h). The plastic layer (Figure 5g) contains more HDPE than the corresponding coal layer (Figure 5h). Furthermore, the odd/even mass ratio is higher for the coal layer, suggesting that it contains more heteroatomic species. This is consistent with the FTIR results. A simple quantitation method was tried with the FIMS data (Table 4), and it appears to work fairly well (to the extent determinable at this stage). This method is compared with another method below.

In Table 5, the results of two methods for estimating the concentration of HDPE in liquefaction process streams are compared. In the first method, the THF-insoluble content of a PFL sample was measured and assumed to be unconverted HDPE. In the second method, a linear relationship between the HDPE concentration and the number average molecular weight (M_N) determined by FIMS was assumed. The methods for this limited sample set agree quite well. The FIMS approach offers the potential to quantify the amount of unconverted HDPE present in the bottoms (PFC) stream. This would allow a more accurate determination of HDPE conversion than is presently available.

Conversion of HDPE During Run CMSL-8

CONSOL and others have found indications that high-density polyethylene (HDPE) is less reactive than coal and other plastics feedstocks toward liquefaction at conventional liquefaction conditions. Since adequate conversion of HDPE is an important factor in the development of coal/plastics coprocessing, it is important to know the conversion of the HDPE during Run CMSL-8 and other coal/plastics coprocessing runs. Upper limits for both single-pass and overall conversions of HDPE during Run CMSL-8 were estimated (Table 6). It was assumed that: 1) the HTI unit was operating at steady-state, 2) that the PFL THF-insolubles are HDPE, and 3) that there was no unconverted HDPE in the PFC. During Run CMSL-8, PFL was both the recycle liquid (Figure 1) and a liquid product. Overall conversion is a measure of fresh HDPE which is not present as unconverted HDPE in the net products; in overall HDPE conversion, recycled HDPE is considered an internal stream and does not need to be explicitly accounted

for. The single-pass conversion of HDPE is a measure of the disappearance of both the recycled and fresh HDPE fed (recycled HDPE is explicitly accounted for).

The conversion calculations require material balance data for the HTI run periods,[3] and an estimate of the amount of HDPE in the pressure-filter liquid (PFL). Details of the method used are provided elsewhere.[7] These results (Table 6) represent an upper limit for conversion, because the HDPE concentration in the pressure-filter cake (PFC) product could not be determined. The overall conversion of HDPE ranged from 40-80% during the run (Table 6), lower than the 90-95% coal conversion and 80-85% resid conversion typically observed for coal liquefaction. The single-pass HDPE conversions averaged around 25%. Both overall and single-pass conversions were lowest during period 16, after an increase in second-stage reactor temperature and space velocity. Measures taken by HTI to improve performance after period 16, such as reducing the space velocity and doubling the dispersed Mo catalyst concentration, restored the conversions observed in period 11. The single-pass HDPE conversion in period 22 was much higher at about 50%. Measures that HTI took to maintain operability in that period of the run when HDPE and coal were fed seemed to provide the high single-pass conversion, and high overall conversion of HDPE.

Conclusions

The major conclusions from characterization of Run CMSL-8 samples are listed below.

- PS products are identifiable and quantifiable in the SOH distillate product from coal/mixed plastics co-liquefaction.
- HDPE appears to be an important source of n-paraffins in the SOHs from coal/plastics co-liquefaction.
- The SOH sample from period 9 in which the on-line hydrotreater was by-passed was much poorer in quality than the SOHs produced with the hydrotreater in operation.
- Identification of some PS and polyethylene terephthalate (PET) products in the SOHs may be masked by highly effective on-line hydrotreating. Addition of a hydrotreater feed sample point, or of more off-line hydrotreater reference periods may help in identification of plastics liquefaction components in the SOHs.
- Incompletely converted HDPE constituted 15 to 30 wt % of the PFL recycle streams, and was found as THF insolubles; virtually no THF insolubles were present in the coal-only period PFL.
- Phase separation in some PFL distillation resids indicates that HDPE products have complex phase behavior.
- HDPE conversions were estimated to be ca. 80 % overall, and ca. 25 % single-pass, and the conversions were responsive to changes in process conditions.
- THF insolubility is currently the best way to separate HPDE in liquid samples which contain no other solids.
- FTIR is useful for the identification of HDPE products.
- FIMS allows distinction of coal-derived material and HDPE-derived material in process stream samples. Quantification of HDPE seems possible using the FIMS technique, but additional development is needed.

PLANS:

CONSOL Support to DOE Coal/Plastics Co-Liquefaction Development

We will do similar sample collection, distribution, and characterization work for future runs. Specialized analyses will supplement baseline characterization techniques. Additional analytical work, such as method development and evaluation, will be performed, as needed, to address key issues in coal/waste coprocessing. This will include evaluation of methods for characterization of plastic liquefaction products. Additional work could include development of alternative liquefaction work-up schemes to accommodate plastic components which are not amenable to conventional coal liquefaction work-up schemes. It is anticipated that at some future point, a distillate product oil from coal/waste co-liquefaction will be selected by DOE for a full set of product inspection tests. CONSOL will assist DOE in conducting these tests.

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REFERENCES:

1. Robbins, G. A.; Brandes, S. D.; Winschel, R. A.; Burke, F. P. "A Characterization and Evaluation of Coal Liquefaction Process Streams, Quarterly Technical Progress Report October 1 through December 31, 1994", DOE/PC 93054-10, May 1995.

2. Robbins, G. A.; Winschel, R. A.; Burke, F. P. "Characterization of Coal/Waste Coprocessing Samples from HRI Run POC-2", Prepr. Am. Chem. Soc., Div. Fuel Chem., 40 (1) 1995, Anaheim, CA, April 2-7, 1995, pp. 92-96.

3. Pradhan, V. R. "Run CMSL-8, Evaluation of Coal-Plastics Co-Liquefaction in CTSL Mode", Draft HTI Report, January, 1995.

4. Larsen, J. W.; Lapucha, A. R. "Coal Liquefaction Process Streams Characterization and Evaluation, The Application of ^{252}Cf-Plasma Desorption Mass Spectrometry to Analysis of Direct Coal Liquefaction Heavy Products", DOE/PC 89883-58, October 1992.

5. Malhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation, Characterization of Coal Liquids by Field Ionization Mass Spectrometry and Iodotrimethylsilane Derivatization", DOE PC 89883-39, January 1992.

6. Malhotra, R.; McMillen, D. F. "Coal Liquefaction Process Streams Characterization and Evaluation, FIMS Analysis for Direct Coal Liquefaction Process Streams", DOE/PC 89883-91, March 1994.

7. "A Characterization and Evaluation of Coal Liquefaction Process Streams", Status Report for April 1 through 30, 1995, DOE/PC 93054-13, May 26, 1995.

TABLE 1. RUN CONDITIONS AND PROCESS PERFORMANCE SUMMARY FOR HTI RUN CMSL-8 (227-85)

Condition	1	2	3	4	5
Period No.	6	11(b)	16	20	22
Hours of Run (End of Period)	144	264	384	480	528
wt % Plastics in Feed (a)	0	25	25	33	33
Stage 1 Cat. Age, lb Feed/lb Cat	252	457	711	884	966
Stage 1 Feed Space Velocity lb Feed/hr/ft^3 Reactor Vol.	32.2	29.6	39	30.1(c)	29.6
Oils/Solids Ratio	1.5	1.6	1.8	2.1	1.9
Temperature, °F					
Stage 1	810	810	810	810	810
Stage 2	830	830	850	850	850
HTU	715	715	715	715	715
Dispersed Mo Concentration, ppm of Dry Feed	100	100	100	200(c)	200
Total Material Recovery, % (Gross)	102.2	98.4	96.7	101.2	99.6
Estimated Normalized Yields, wt % MAF Feed					
C_1-C_3 in Gases	11.35	9.14	9.02	7.41	5.17
C_4-C_7 in Gases	4.81	3.27	3.41	3.17	3.27
IBP-350 °F	15.86	20.48	19.00	17.63	8.80
350-500 °F	17.99	12.57	8.59	11.16	7.60
500-650 °F	21.14	19.85	12.27	16.88	10.72
650-850 °F	10.18	11.84	15.18	11.54	14.24
850-975 °F	2.29	2.94	5.60	4.22	6.43
975 °F	4.74	10.53	17.15	19.67	33.83
Unconverted Feed	3.90	4.07	4.50	4.40	4.22
Water	9.04	7.34	6.90	5.92	4.85
COx	0.67	0.80	0.86	0.57	0.16
NH_3	1.50	1.08	1.04	0.82	0.27
H_2S	3.98	2.98	2.84	2.52	2.24
Hydrogen Consumption	7.46	6.91	6.35	5.71	1.80
Process Performance					
Feed Conversion, wt % MAF Feed	96.10	95.90	95.50	95.60	95.80
975 °F$^+$ Conversion, wt % MAF Feed	91.40	85.40	78.40	75.90	62.00
C_4-975 °F Distillates, wt % MAF Feed	72.30	71.00	64.00	64.40	51.00
Hydrogen Efficiency, lb Dist/lb H_2	9.69	10.27	10.08	11.28	28.33

Feeds:
Illinois No. 6 Crown II Mine coal, HDPE, Polystyrene, and PET
Back Pressure: 2500 psig

Catalysts:
K-1: Shell 317 Supported + Dispersed Sulfated Fe/Mo Oxide (100 ppm Mo)
K-2: Only Dispersed Sulfated Fe/Mo Oxide Introduced in Feed to K-1
Hydrotreater: HRI-6135 (Criterion C-411 Trilobe)

(a) Conditions 2-4 used a 50/35/15 w/wt % ratio of HDPE/PS/PET; Condition 5 used HDPE alone w/coal.

(b) Although not specifically listed here, in period 9 the on-line hydrotreater (HTU) was by-passed; otherwise conditions were the same as in period 11.

(c) The total space velocity was reduced from 40 to 30 beginning in Period 18 as a result of operating difficulties at higher space velocities; the dispersed catalyst addition rate also was increased from 100 ppm Mo to 200 ppm Mo beginning in Period 19 to improve process performance.

TABLE 2. CONSOL ANALYSES OF SAMPLES
FROM HTI COAL/PLASTICS CO-LIQUEFACTION RUN CMSL-8

Sample Description; Name (Abbrev.); Sample Point	Periods	Technique & Information Sought (Refer to Key)
Product Distillate; Separator Overheads (SOH); SP-4	6,9,11,16,20,23	A,B,C
Recycle Oil; Pressure Filter Liquid (PFL); SP-6	6,11,16,20,22	A,E,F,G; THF Extract - B; THF Insols - D; Dist. - A,B,E; Resid - G; Resid THF Extract - A,B,H
Solid Residue; Pressure Filter Cake (PFC); SP-7	6,11,16,20,22	G; THF Extract -A,B,H

KEY TO TECHNIQUES AND INFORMATION SOUGHT:

A = ^{1}H-NMR for hydrogen distribution (7 classes), aromaticity (degree of hydrogenation), paraffinicity, hydrogen donors
B = FTIR in THF solution for phenolic -OH content
C = GC-MS for composition, carbon numbers of paraffins
D = special analyses
E = microautoclave test with standard coal for donor solvent quality
F = 850°F distillation for distillate content
G = THF extraction and ash for resid, ash and IOM content, for coal and resid conversion
H = solvent fractionation (oils, asphaltenes, preasphaltenes) for resid composition.

TABLE 3. QUANTITATION OF POLYSTYRENE LIQUEFACTION PRODUCTS IN SOH PRODUCT OILS FROM HTI RUN CMSL-8

Period	Analysis by GC-MS, Area % of SOH Total Ion Chromatogram			Analysis by ^{1}H-NMR	wt % PS in Dry Feed	SOH Yield, wt % of Dry Feed	EB+IPB by GC-MS, as wt % of PS Fed	EB by ^{1}H-NMR, as wt % of PS Fed
	Ethylbenzene, Ret. Time ca. 16.7 min.	Cumene (Isopropylbenzene), Ret. Time ca. 21.8 min.	Total, Area % (assumed to equal wt % of SOH)	As Ethylbenzene, wt % from Integration of Peak at 7.1 ppm				
6 (Coal)	0.55	-	0.55	-	0	50.06	- (b)	-
11 (Coal/Mixed Plastics)	6.53	1.91	8.4	8.8	8.75	47.65	45.7	47.9
16 (Coal/Mixed Plastics)	8.32	3.38	11.7	15.1	8.75	33.52	44.8	57.8
20 (Coal/Mixed Plastics)	6.94	2.01	9.0	12.1	11.55	43.28	33.7	45.3
23 (Coal/HDPE)	1.38	0.29	1.7	3.4	0	25.29	(c)	(d)
9 (Coal/Mixed Plastics - HTU Off-line)	13.52	4.03	17.6	15.4 (a)	8.75	35.02	70.4	61.6

(a) Assumed 11 wt % H in SOH for NMR estimate, other periods used wt % H reported by HTI.[3]
(b) Represents 0.3 wt % of dry coal fed; equivalent to 3.1 wt % of PS fed in period 11.
(c) Represents 0.6 wt % of dry coal fed; equivalent to 3.7 wt % of PS fed in period 20.
(d) Represents 1.2 wt % of dry coal fed; equivalent to 7.4 wt % of PS fed in period 20.

TABLE 4. ESTIMATION OF HDPE CONCENTRATION WITH FIMS DATA

Sample	FIMS M_N, Da	FIMS M_W, Da	Estimate of wt % HDPE[a]	M_W/M_N
HDPE	154	558	100	3.6
PFL 22 THFI[b]	184	662	93	3.6
PFC 22	304	591	66	1.9
PFL 22	329	493	14[c] (61[d])	1.5
PFL 11 Resid Top Layer	404	627	44	1.6
PFL 11 Resid Bottom Layer	466	580	30	1.2
THF-Soluble Coal Resids[4,5]	600	710	-	1.2

Note: FIMS analyses were performed by R. Malhotra, at SRI International.

(a) It was assumed that wt % HDPE is linearly related to M_N, and that M_N = 154 Da for 100% HDPE, and M_N = 600 Da for 100% coal resid.[4,5]
(b) THFI = THF insolubles.
(c) It was assumed that M_N = 515 Da for the non-HDPE portion of the sample, rather than 600 Da, as in the other samples. This value was calculated from 21.1 wt % of the THF-soluble PFL as 850 °F$^-$ distillate with an assumed M_N = 200 Da, and 78.9 wt % of the THF-soluble PFL as 850 °F$^+$ resid with an assumed M_N = 600 Da.
(d) Value if uncorrected for 850 °F$^-$ distillate.

TABLE 5. COMPARISON OF METHODS TO ESTIMATE HDPE CONCENTRATION

Sample	Estimate of HDPE as THF Insolubles, wt % of Sample		Estimate of wt % HDPE, Based on M_N
	From Whole Sample	From Resid	
PFL 22 THFI	100	-	93
PFL 22	18.6	15.8	14
PFL 11 Resid Top Layer	-	-	44
PFL 11 Resid Bottom Layer	-	-	30
PFL 11	20.0	20.3	23[a]

(a) Calculated from wt % HDPE in each resid layer, the wt % of each layer in the resid (66.7 wt % top layer, 33.3 wt % bottom layer), and 59.3 wt % resid in the PFL.

TABLE 6. OVERALL AND SINGLE-PASS CONVERSIONS OF HDPE DURING HTI RUN CMSL-8

Period	wt % HDPE in PFL [a]	Overall Conversion, % [b]	Single-Pass Conversion, % [b]
Using THF insolubles in whole PFL as estimate for HDPE in PFL:			
11	20.0	80.7	23.2
16	30.4	44.6	9.1
20	14.5	71.6	26.2
22	18.6	73.9	49.5
Using THF insolubles in PFL resid as estimate for HDPE in PFL:			
11	20.3	80.5	22.9
16	37.4	32.0	5.9
20	16.5	67.7	22.9
22	15.8	77.8	53.3

(a) Assuming that THF insolubles in PFL are unconverted HDPE.
(b) Calculations are described in Reference 7.

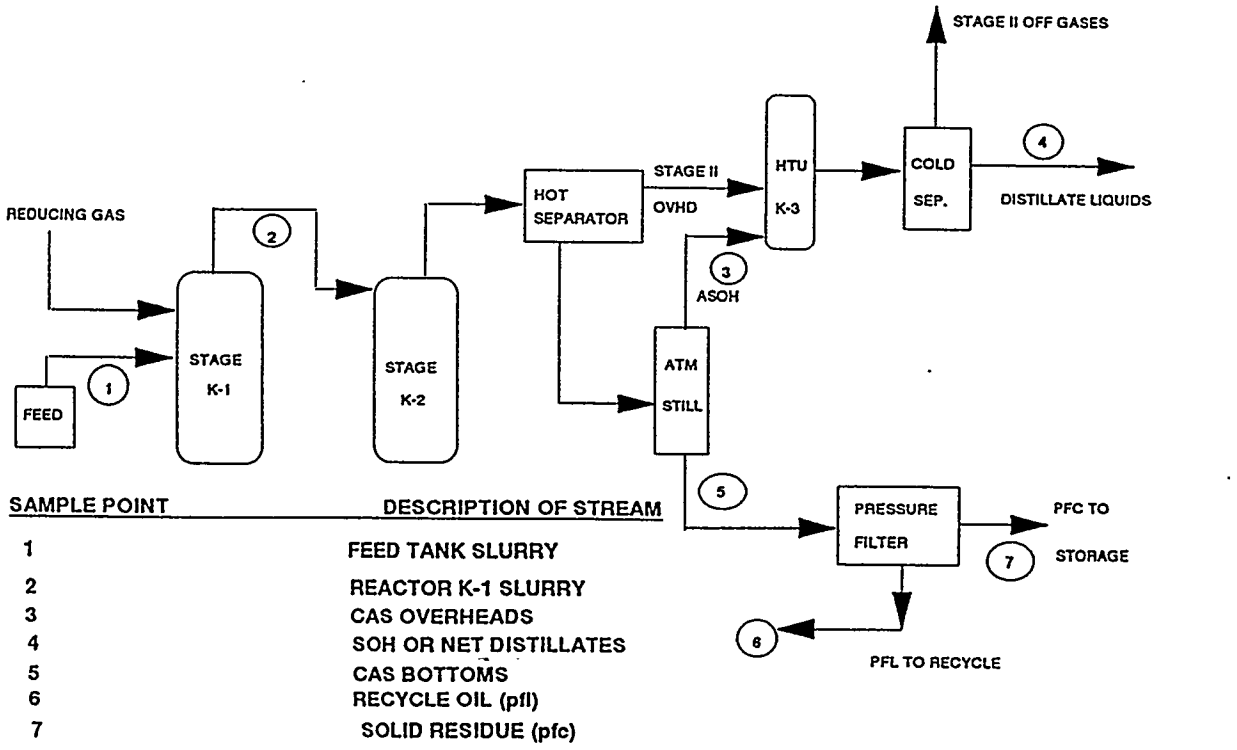

Figure 1. Simplified Plant Diagram for HTI Run CMSL-8.
(Source: Reference 3)

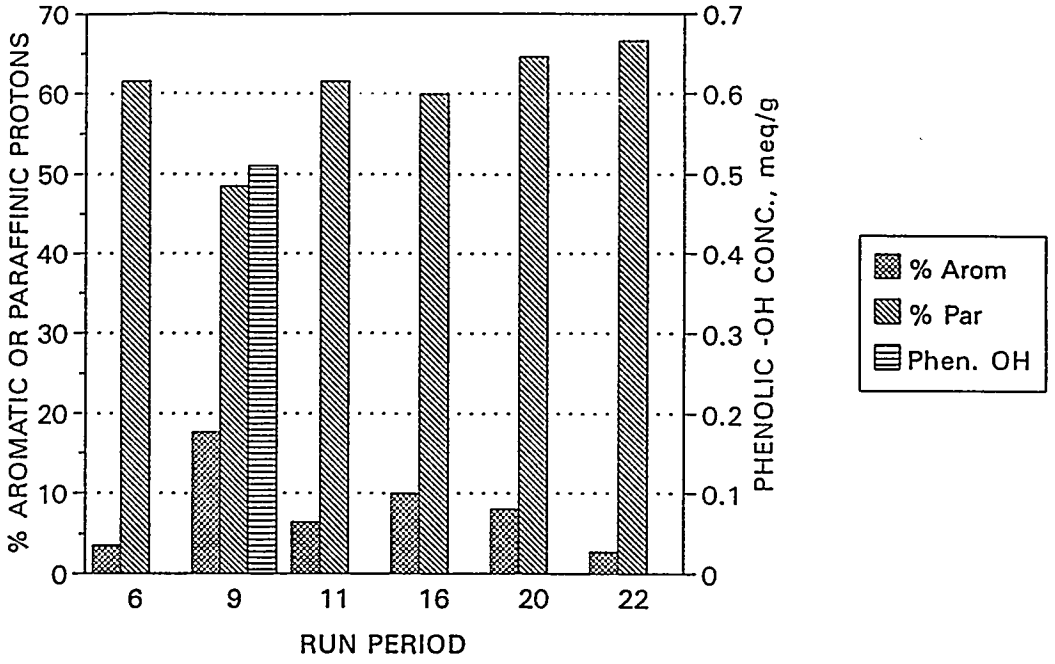

Figure 2. Characteristics of SOH Samples from Run CMSL-8.

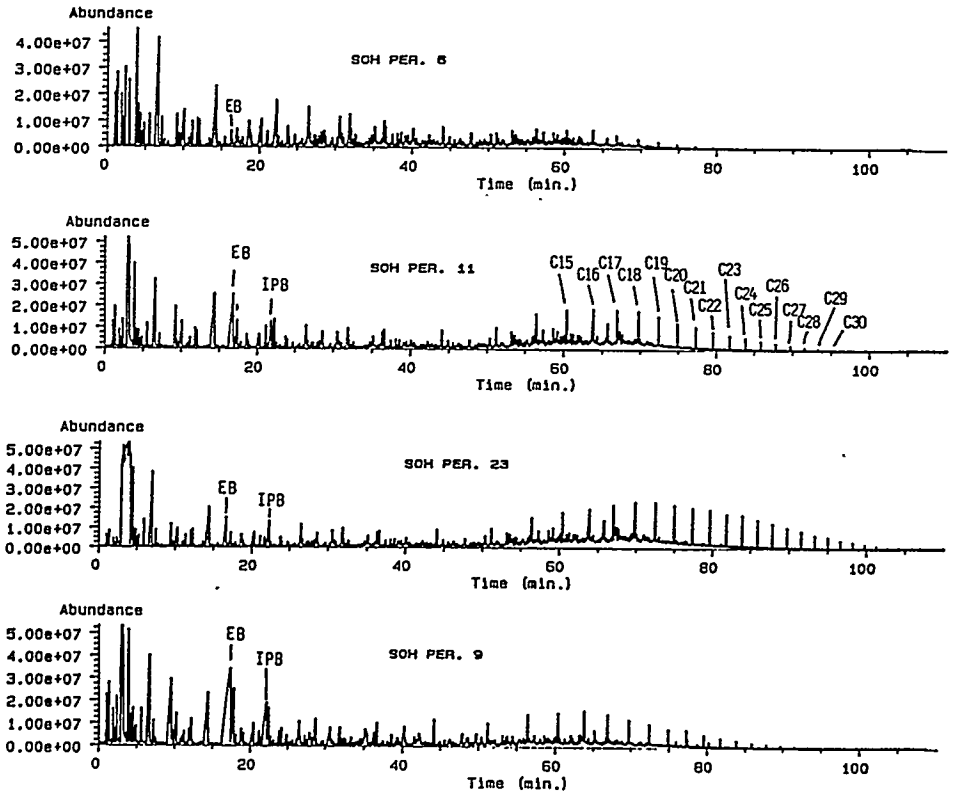

Figure 3. Gas Chromatography-Mass Spectrometry (GC-MS) Total Ion Chromatograms of Selected SOH Samples from Run CMSL-8.

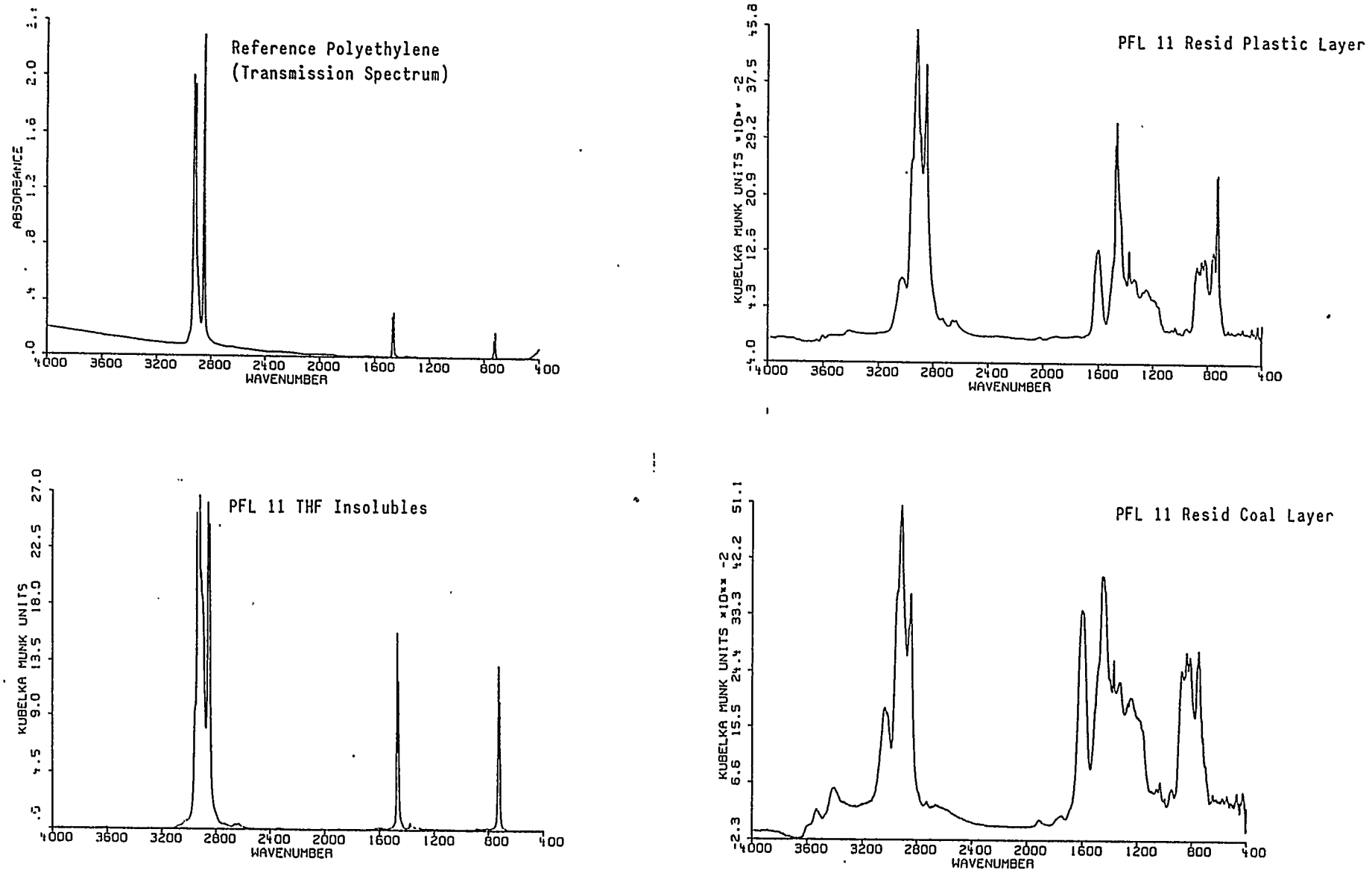

Figure 4. Fourier-Transform Infrared (FTIR) Spectra of Reference Polyethylene and Selected Run CMSL-8 Samples.

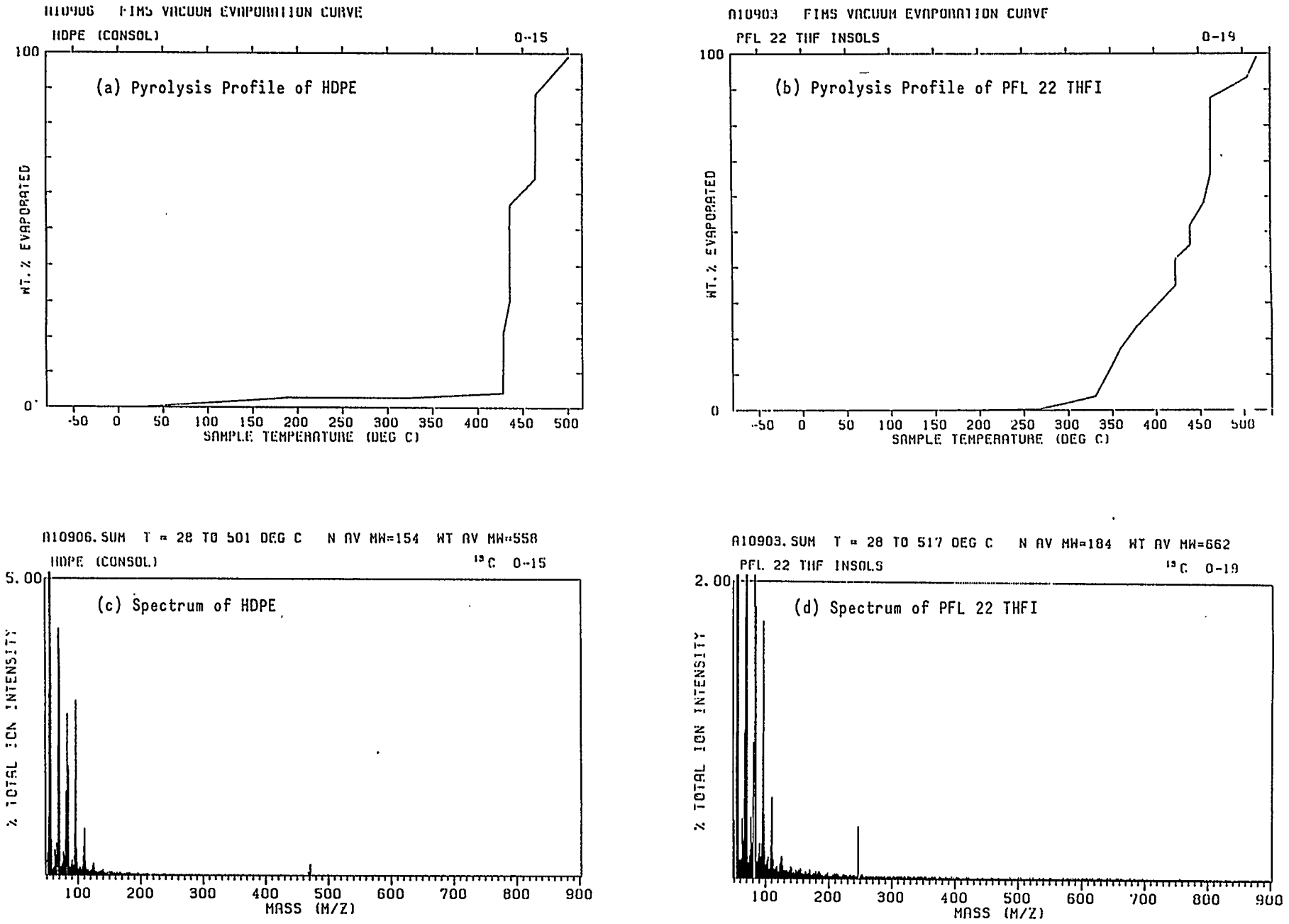

Figure 5. Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

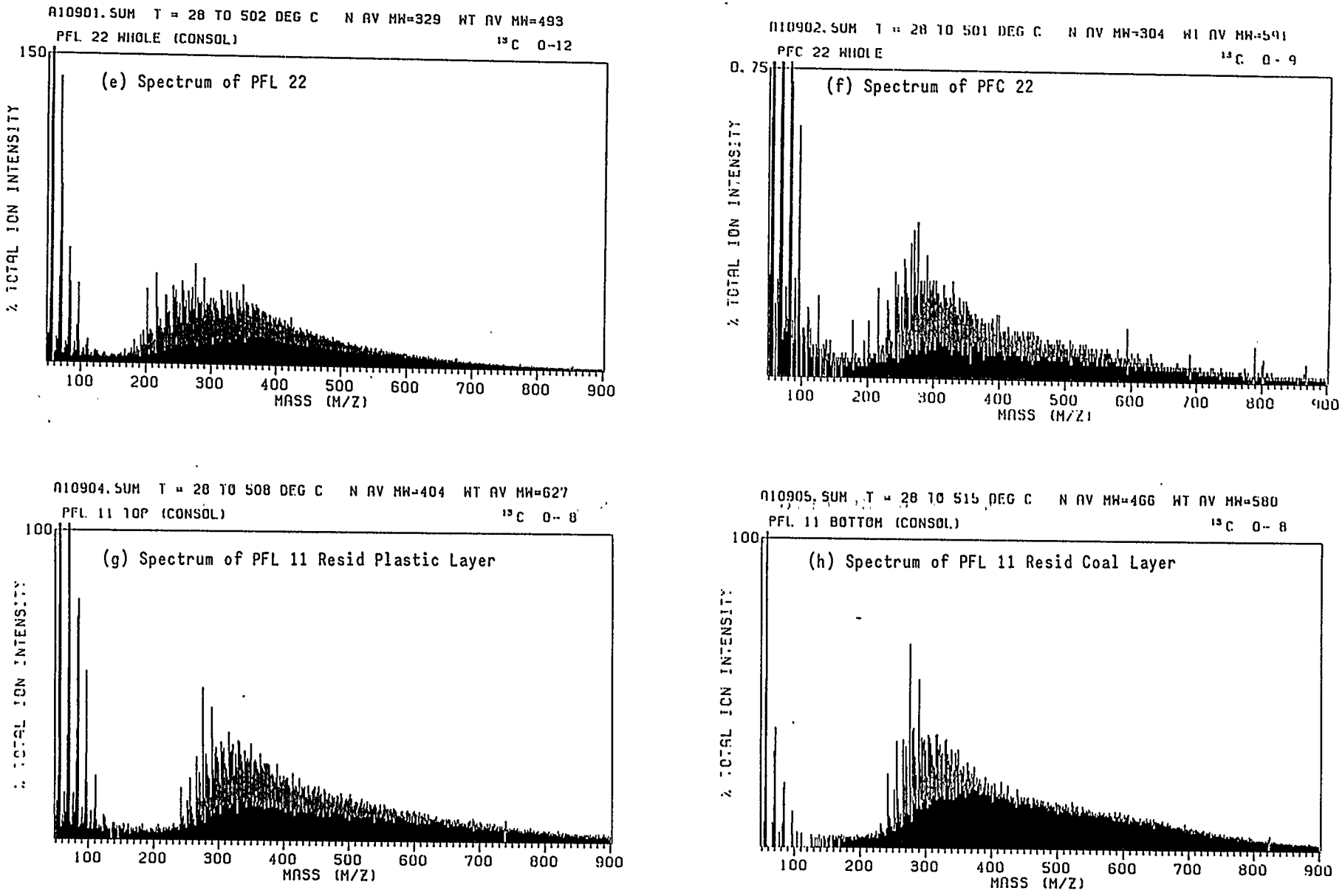

Figure 5 (Continued). Pyrolysis Profiles and Field-Ionization Mass Spectrometry (FIMS) Spectra of Selected Run CMSL-8 Samples.

APPENDIX 7

ABSTRACT FOR 9TH ANNUAL TECHNICAL MEETING OF CFFLS
August 15-18, 1995

CHARACTERISTICS OF PROCESS OILS FROM HTI COAL/PLASTICS CO-LIQUEFACTION RUNS

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ABSTRACT

Coal and plastics were co-liquefied in three recent DOE-sponsored HTI runs at the bench and PDU scales. Feedstocks included coal alone, coal/mixed plastics, and coal/polyethylene. CONSOL analyzed process stream samples from representative periods of these runs to provide information about the chemical transformations of the feedstocks and their distribution in recycle and product streams. Substantial quantities of identifiable products of polystyrene were found in distillate product oils from coal/mixed plastics processing. Furthermore, the coal/plastics product oils from Run CMSL-8 contained relatively more and relatively longer chain n-paraffins than the corresponding coal-only product oil, based on GC/MS chromatographic data. The additional n-paraffins thus appear to be produced primarily from liquefied polyethylene. Recycle and bottoms stream samples from coal/plastics operating periods were found to have unusual characteristics when analyzed using common coal liquefaction workup procedures. The unusual characteristics result from plastics having properties which are atypical of coal-derived materials, and are brought to prominence by the low conversion of high-density polyethylene. Characteristics of these co-liquefaction materials by standard and non-standard analytical techniques will be presented. Implications for coal/plastic co-liquefaction processing and for analysis of samples from these processes will be discussed.

APPENDIX 8

UNIVERSITY OF DELAWARE PAPER FOR 210TH NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY

A NOVEL METHOD FOR THE DETERMINATION OF THE BOILING RANGE OF LIQUID FUELS BY THERMOGRAVIMETRIC ANALYSIS

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Key words: boiling range, liquid fuels, SimDis TGA

INTRODUCTION

The most widely used separation technique in the petroleum industry as well as in much of the chemical industry is distillation. This is particularly true of all liquid fuel production processes, including coal-derived liquid fuels, and shale oil as well as petroleum. To design and operate a suitable distillation column system requires a knowledge of the boiling point distribution of the materials to be separated. In recognition of this need, the ASTM developed the classical distillation procedures of ASTM D86, D216, D447, D850, and D1078. Since these methods required a relatively large sample and are not particularly precise, the widely used simulated distillation analysis based on gas chromatography (ASTM D3710-83) was introduced. This method requires only a small sample size and is reasonably rapid. However, it is limited to materials boiling below about 350°C. Above that temperature the column packing becomes unstable and the materials being analyzed tend to crack. Also the results measured by the SimDis GC method are determined by the interactions between the tested sample and the selected column packing. Therefore the GC method is not fundamentally a determination of the boiling range of the sample mixture but rather a measure of the range of interactions of the sample with the packing.

To avoid the limitation in the higher boiling range of the tested material in the SimDis GC method, Schwartz et al developed a capillary supercritical fluid chromatography (SFC) method (1). When the SFC is properly calibrated, it has been shown to be a suitable simulated distillation method, even for materials having atmospheric equivalent boiling points as high as 760 °C or 1400 °F. However this does not eliminate the problem of interactions of the sample with the packing material.

In their work, Schwartz et al also used both atmospheric "flow" thermogravimetric analysis (FTGA) and vacuum thermogravimetric analysis (VTGA) methods to distinguish between evaporation and thermal decomposition. They have observed a bimodal distribution of DTG (the rate of weight loss) on Arabian heavy atmospheric residue in both FTGA and VTGA runs. The first peak in the VTGA (about 0.2-0.5torr) profile is shifted towards lower temperature as compared with the FTGA profile since the sample vaporization was enhanced by a reduced pressure. However, the reduced pressure had no effect on the position of the second peak in the VTGA curve since the thermal decomposition or pyrolysis rate was not significantly affected by the reduced pressure. Therefore, the low temperature peak in each DTG curve is interpreted as the sample vaporization profile and the high temperature peak as the thermal decomposition or pyrolysis reactions.

In the investigation of the hydrocracking of high boiling coal derived vacuum resids, it became important to measure the degree to which the resids had been broken down to lower boiling products. This plus the importance of a simple, rapid, and accurate analytical distillation technique mentioned above motivated the development of an analytical TGA method for boiling range measurement, i.e. atmospheric equivalent boiling point (AEBP) curve, of a variety of samples. While supercritical chromatography was an alternative, the use of thermogravimetric analysis to determine the AEBP curve was an attractive approach. Such a SimDis TGA method would not be affected by interactions with column packing and not limited by sample boiling point range. Development of this novel SimDis TGA method and the preliminary results on a variety of samples are presented in this paper.

EXPERIMENTAL

TGA Apparatus. A horizontal thermogravimetric analyzer (TGA), TA Instruments model 51 (New Castle, Delaware), was used. In this particular instrument, dual thermocouples were used for the system temperature control. One is a furnace thermocouple and the other is a sample thermocouple, which is located very close to the test sample. The sample thermocouple is always used for the temperature measurements. Only the furnace thermocouple is used for control in the ramp method (constant heating rate). However, either the furnace thermocouple or the sample thermocouple can be used for isothermal control, depending on the purpose. If the "Isothermal" mode is selected, the

furnace thermocouple is used. On the other hand, if the "Isotrack" mode is selected, the sample thermocouple is used. The isotrack mode gives much better temperature control, for example, ± 0.01 to ± 0.05 °C for the range of 60 to 280 °C, compared to the Isothermal mode.

Nitrogen was used as an inert carrier gas at 100 ml/min volumetric flow rate. Vacuum TGA (VTGA) was carried out by attachment of the thermogravimetric analyzer to a vacuum pump. A vacuum gauge from 0-760 mmHg (0-1 atm.) range was used to monitor the pressure. After a sample was loaded onto the sample pan, the vacuum metering valve (shown in Figure 1) was gradually opened, and the pressure was adjusted to a predetermined value (down to 30 mmHg or 0.0395 atm). By this control and use of a ballast tank (buffer), the pressure (or vacuum) of the TGA chamber was found to be very stable during the VTGA analysis.

TGA Sample Pan. The SimDis TGA method requires a change in the conventional TGA sample pan because the rate of weight loss in the open pan system is controlled not only by the vapor pressure of the test sample but also by mass transfer. The TGA sample characteristics in the pan as well as the diffusion out constantly change with the sample amount as the TG analysis proceeds. For those reasons, a new sample pan configuration with a small aperture at the top, as shown in Figure 2, was devised. The objective of this change is to make the rate of the weight loss from the sample pan primarily determined by the partial pressure of the sample molecules. This partial pressure has been shown from thermodynamic considerations and experimentation to be essentially equal to the vapor pressure of the sample. Three cylindrical quartz TGA sample pans with different sizes of circular aperture at the top were fabricated. The diameters of the apertures were 0.615, 0.974, and 1.538 mm. In each TGA test, about 80 mg of liquid sample was injected into the sample pan by a syringe before the TG analysis.

SimDis TGA Methods. Analytical variables, such as carrier gas flow rate, pressure, and temperature or heating rate, were held constant during a TG analysis. Two methods, i.e., a ramp method and an isotrack method, have been used in the SimDis TGA technique. In the ramp method, a constant heating rate was used and the rate of the weight loss determined versus temperature. In the isotrack method, the temperature of the sample is very rapidly heated to a predetermined temperature within 2 minutes, and precisely controlled at this preset temperature within 0.01 to 0.05 °C after 5 minutes. The weight change and the DTG (the differential of the weight loss curve) decay are determined as a function of time.

Materials Studied. A light paraffinic vacuum distillate from Amoco and a converted resid liquid were used to test the SimDis TGA technique.

SimDis TGA Calibration. A SimDis TGA system can be calibrated by either a synthetic mixture which contains compounds of known boiling range or a 'standard' mixture for which distillation curves are available. In either case, the calibration sample should be similar to the sample for which the boiling range is to be determined. For the synthetic mixture, the paraffins, especially n-alkanes, provide a wide range of boiling components for calibration purposes. For the 'standard' mixture, any petroleum sample with known boiling range distribution could be selected. Some variation between samples of the same boiling point but different chemical structure are to be expected due to variation in molecular characteristics (such as molecular weight and shape) and heats and entropies of vaporization of the samples.

n-Alkane standards, C-10 to C-32, were purchased from Aldrich Chemical Co (Milwaukee, NJ). The SimDIS TGA was calibrated with a synthetic mixture of these n-alkane standards shown in Table 1.

SimDis TGA Data Processing. The smoothed and noise-free DTG curves were acquired by an 11 point smoothing technique (2).

RESULTS AND DISCUSSION

Strategies for Selection of the Optimum Method for Determining Boiling Point Range of an Unknown Sample. The analytical variables of the SimDis TGA technique include: 1). time-temperature profile: ramp method or isotrack method; 2). pressure: atmospheric pressure or under vacuum (down to 0.03 atm.); 3). size of the aperture at the top of the pan; and 4). carrier gas type and flow rate.

For a pure compound. SimDis TGA can be run using either the ramp or isotrack method. For an unknown mixture, the ramp method provides information concerning the vaporization range of the sample. If run under at least two pressures (vacuum), it can distinguish quantitatively between the material boiling so high that pyrolysis will occur and that fraction volatilizing under distillation conditions.

To accurately obtain the boiling range curve for a mixture, the isotrack method is the preferred technique. This method translates the decay of the rate of weight loss into the boiling point distribution. Therefore, the optimum conditions to run a simulated distillation by TGA are those conditions which give the highest sensitivity and stable decay curve. To accomplish this, the optimum conditions for a SimDis TGA run is dependent on the boiling range of the test sample. For example, for light samples, it is better to run the SimDis TGA at a low isotrack temperature, small hole size of pan, and atmospheric pressure. For very high boiling mixtures, SimDis TGA should be run at a higher isotrack temperature, larger hole size of pan, and high vacuum (for example, 30 mmHg). For a mixture containing a very broad boiling range, the test can be run at either more than one temperature or more than one pressure (vacuum) or both to detect the very volatile fraction as well as the higher boiling components.

The recommended general steps to run an unknown sample using the SimDis TGA technique are:

1). ramp at 1 to 5 °C/min to 600 °C at 1 atm and/or under vacuum (down to ca. 0.03 atm.) at 100 cm^3/min N_2. Oxygen is then introduced to burn off the combustible material remaining (if any). In this run, IBP (Initial Boiling Point), FBP (Final Boiling Point) and/or PT (Pyrolysis Temperature), the boiling range and volatile fraction, and ash fraction (if any) are determined.

2). based on the results obtained from Step 1, select the optimum conditions of aperture size of pan, isotrack temperature, pressure, etc. to run a SimDis TGA.

SimDis TGA by the Ramp Method. Typical DTG curves from SimDis TGA runs using the ramp method at two pressures on a light paraffinic vacuum distillate from Amoco are shown in Figure 3. The rate-of-weight-loss curves show a distinct shift to lower temperatures as the pressure is reduced. No pyrolysis is evident in this determination since the DTG curve is entirely shifted under vacuum. The volatilization range for this sample at atmospheric pressure is between about 200°C and 470 °C. Under the vacuum of 0.238 atm., it is shifted to between about 180°C and 420 °C. The volatilization ranges are somewhat lower than the actual boiling range because of the nitrogen gas sweep and controlled diffusion.

SimDis TGA Calibration. Temperature-time plot for a calibration run using a synthetic mixture of hydrocarbons of C_{10} to C_{32} is shown in Figure 4. The predetermined isotrack temperature was 280 °C. The DTG decay curve for this calibration is shown in Figure 5. Although the temperature of the sample reached the predetermined temperature of 280 °C within 2 minutes, the loss of the light fractions in the synthetic mixture, such as C_{10} and C_{15}, occurred before the temperature became stable. In other words, the light fractions in the synthetic mixture of C_{10} and C_{15} were evolved from the sample pan within this initial 2-5 minutes. This is clearly illustrated in Figures 6 and 7, the plot of wt% of sample in the pan vs. temperature and wt% of sample in the pan vs. DTG decay, respectively. From the concentrations of the C_{10}-C_{32} components in the synthetic mixture given in Table 1, we can find the rates of weight loss at which the components were evolved from the pan. The plot which describes a linear relationship of log (rate of weight loss) vs $1/T_b$ (T_b, the boiling point of C_{20}-C_{32}) is shown in Figure 8, in accordance with the Clausius-Clapeyron equation. This shows that the DTG decay determined by TGA technique is indeed measuring the vapor pressure and therefore boiling range.

SimDis TGA Test. For a mixture containing a wide range of boiling materials, such as the light paraffinic vacuum distillate from Amoco, the DTG decay determined under the same conditions of running the calibration mixture can be translated into a boiling range distribution using the equation of

$$T_b = \frac{B}{\ln(r) - A} \qquad (1)$$

where r is the decay rate of the test sample and A and B are parameters determined by calibration (for this case, A = -21.06 and B = 12778).

Temperature-time plot for the test sample of the light paraffinic vacuum distillate is similar to that as shown in Figure 4. The DTG decay curve is shown in Figure 9. Although the temperature of the sample reached the predetermined temperature of 280 °C within 2 minutes, the 10 wt% of light fractions in the vacuum distillate were lost before the temperature became stable, i.e., the 10 wt% of light fractions in the vacuum distillate were evolved from the pan within this initial 2-5 minutes. This is clearly illustrated in Figure 10, the plot of wt% of sample in the pan vs. temperature. The simulated distillation curve for this vacuum distillate is shown in Figure 11.

A simulated distillation run by the isotrack method has been made on a sample of Wilsonville # 258 resid converted using sulfided molybdenum naphthenate at 403°C for 60 minutes. The boiling range curve derived from the DTG decay of this sample is shown in Figure 12. The fraction of material in which the product boiled below 850 °F (the cut-off point for resid) was 93.8 wt% (including tetralin fraction).

Advantages of the SimDis TGA Method. The most significant advantages to using the TGA technique for simulated distillation are:

1). SimDis TGA is run at much lower temperature than other techniques, especially if combined with vacuum.
2). there is no limitation to the sample type. The sample can be very light or very heavy. Even a sample with a very wide range of boiling materials can be tested by this technique.
3). Highly reproducible results can be obtained. The experimental cycle for one run can be 1 to 12 hrs, depending on sample and purpose. No cleaning is required as would be necessary in a distillation column.
4). Very small amounts of sample (30-80 mg) are required for each SimDis TGA run;
5). The SimDis TGA method measures the true boiling characteristics of the sample and is not affected by interactions between the test sample and packing, as is the case with the chromatographic methods.

SUMMARY AND CONCLUSIONS

1. Two analytical methods (a ramp and an isotrack method) have been developed for determining the boiling range of an unknown sample based on the use of thermogravimetric analysis.

2. These methods require the use of a special cylindrical sample pan with a small hole in the top to control the rate of weight loss (diffusion of the sample vapors exiting the pan). Under these conditions, the diffusion rate is proportional to the vapor pressure of the sample at the particular temperature of the analysis.

3. For screening an unknown sample, the "ramp method" is used in which the temperature of the sample is increased at a predetermined rate while holding the purge gas flow rate constant. The temperature range of volatilization is measured. If high boiling material is present which involves pyrolysis of the sample rather than only volatilization, a similar "ramp method" is run under vacuum. This indicates which portion of the sample is volatilized and what portion is pyrolyzed under the conditions of the test.

4. For more precise determination of the boiling range of a sample, the isotrack method is used. In this method, the sample is rapidly heated to a predetermined temperature and then held constant while the rate of weight loss (DTG) is measured. When the system is properly calibrated with a known sample, the rate of weight loss (DTG decay) can be translated by a computer program into an actual boiling range.

ACKNOWLEDGEMENTS

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REFERENCES

1. Schwartz, H.E.; Brownlee, R.G.; Boduszynski, M.; Su, F. *Anal. Chem.* 1987, 59, 1393.
2. Wang, Keyu: Huang, H.; Wang, S.; Klein, M.T.; Calkins, W.H.* "A Novel Smoothing Technique for Thermogravimetric Analysis Data", to be submitted to *Anal. Chem.*

Table 1 Concentrations and properties of the C_{10}-C_{32} components in the synthetic mixture

No. of Carbon	Name	MW	b.p.,°C	m.p.,°C	W, g	C, wt%
10	Decane	142.28	174.1	-29.7	1.2298	18.26%
15	Pentadecane	212.41	270.6	10.0	1.2068	17.92%
20	Eicosane	282.54	343.0	36.8	1.1238	16.69%
25	Pentacosane	352.67	401.9	55.0	1.0716	15.91%
30	Triacontane	422.80	449.7	65.8	1.0402	15.45%
32	Dotriacontane	450.85	467.0	69.7	1.0618	15.77%

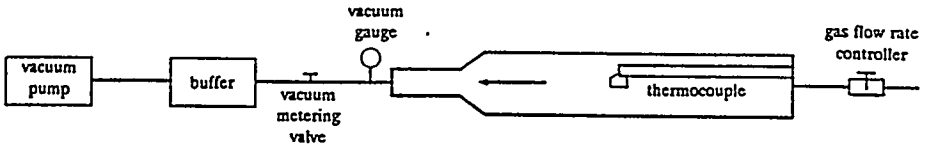

Figure 1 Instrumentation of vacuum thermogravimetric analyzer (VTGA)

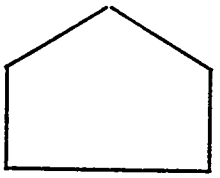

Figure 2 A SimDis TGA sample pan

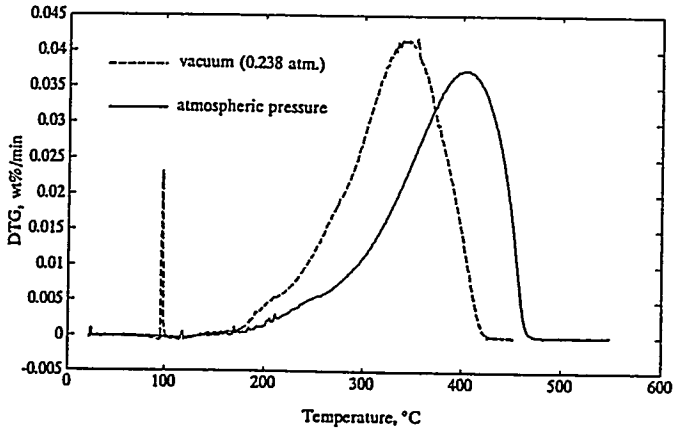

Figure 3 DTG curves from SimDis TGA runs using the ramp method at two pressures on a light paraffinic vacuum distillate from Amoco

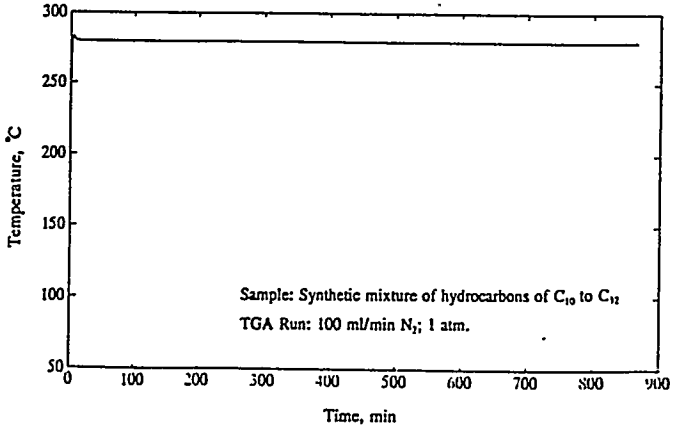

Figure 4 Temperature-time plot for the calibration sample of a synthetic mixture of n-alkanes

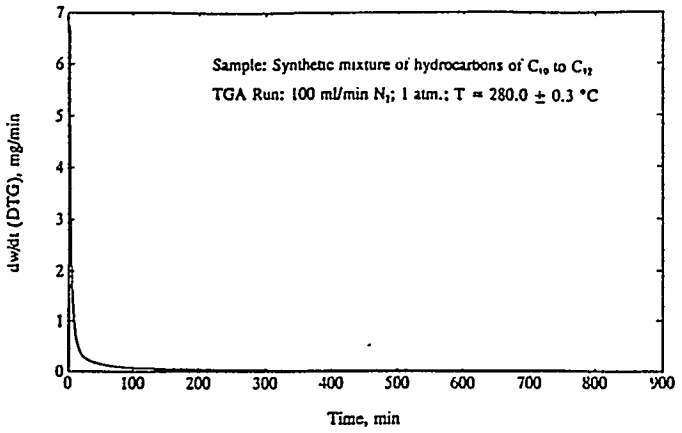

Figure 5 DTG decay curve for the calibration run

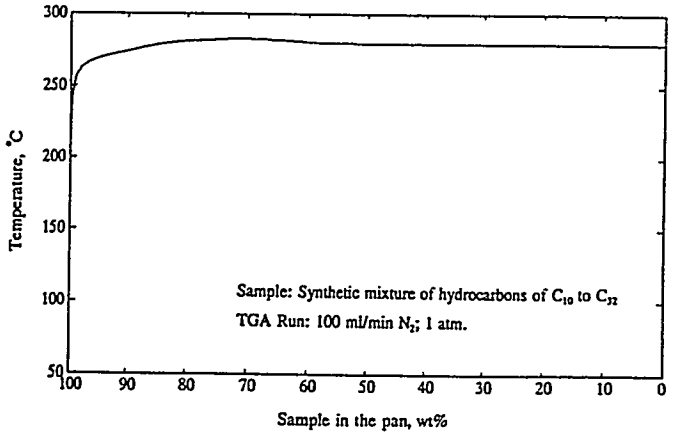

Figure 6 Plot of wt% sample in the pan vs. temperature for the calibration run

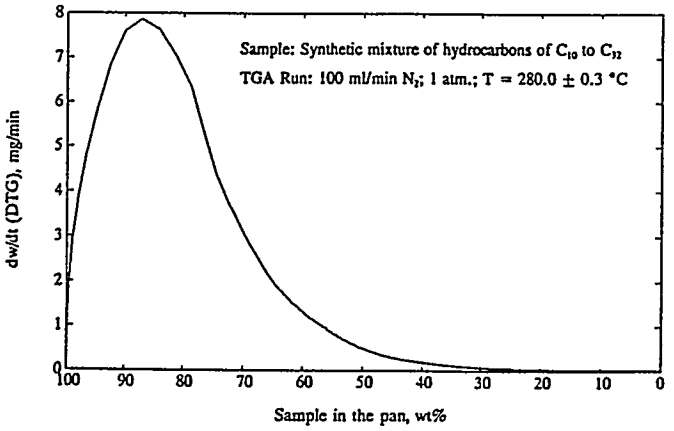

Figure 7 Plot of wt% sample in the pan vs. DTG decay for the calibration run

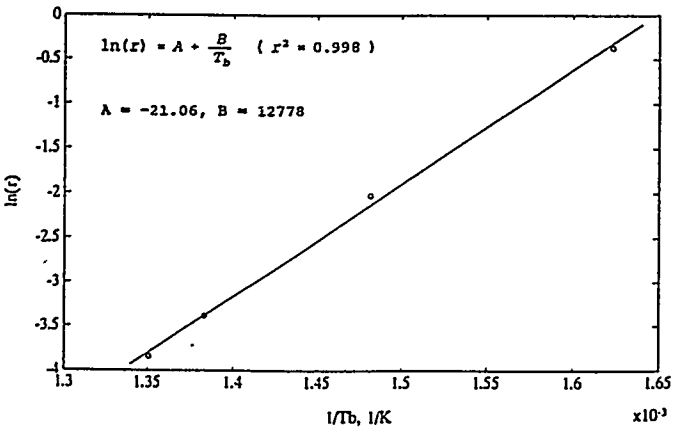

Figure 8 ln(r) vs. $1/T_b$ (r: rate of weight loss; T_b: boiling point of C_{20}-C_{32})

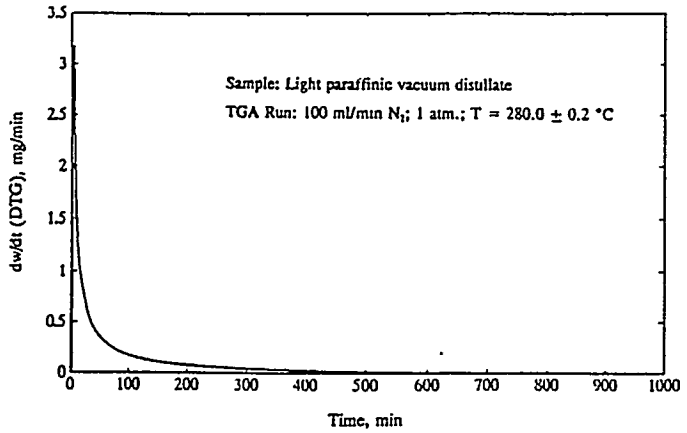

Figure 9 DTG decay curve for the light paraffinic vacuum distillate

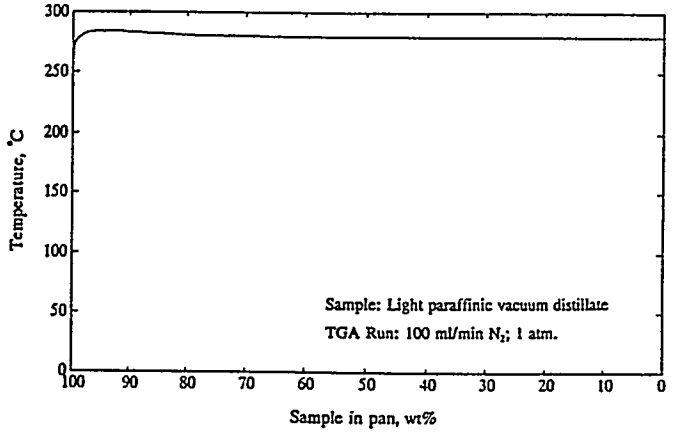

Figure 10 Plot of wt% sample in the pan vs. temperature for the light paraffinic vacuum distillate

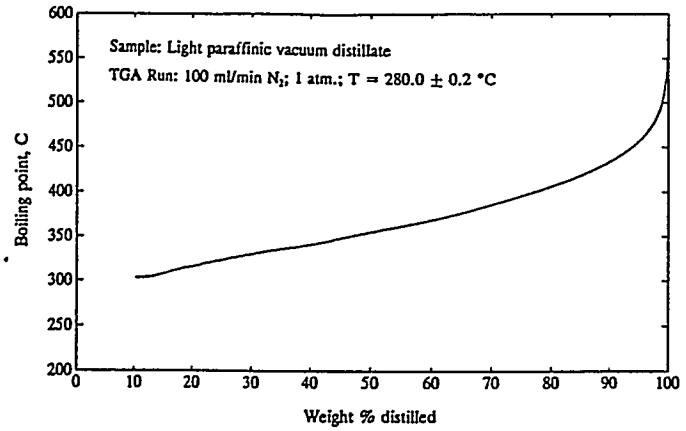

Figure 11 Simulated distillation curve (AEBP) for the light paraffinic vacuum distillate

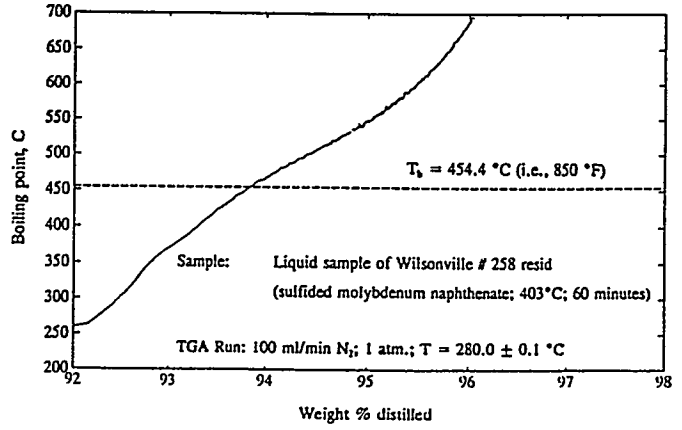

Figure 12 Simulated distillation curve (AEBP) for the liquid sample of a resid conversion run under 1500 psig H_2

APPENDIX 9

PAPER FOR THE TWELFTH ANNUAL INTERNATIONAL PITTSBURGH COAL CONFERENCE

THE ROLE OF PROCESS OIL CHARACTERIZATION IN DIRECT COAL LIQUEFACTION

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ABSTRACT

A process-derived recycle oil is an important feature of a direct coal liquefaction process. The recycle oil is a vehicle to convey coal into the liquefaction reactor. It is a medium for mass and heat transfer among the solid, liquid, and gaseous reactants. It can be a reactant in the process. Because the recycle oil can have a determining effect on process configuration and performance, characterization of its composition and chemistry is of considerable interest. This paper will discuss recycle oil characterization, its influence on the development of coal liquefaction technology, and suggest some future research directions.

EARLY GERMAN TECHNOLOGY

In the early 1900s, Bergius used a petroleum "heavy oil" as a vehicle to slurry coal in batch and continuous unit liquefaction experiments.[1] The German technology utilized in the 1940s was based on further development of the Bergius-Pier process, and utilized high temperature and pressure (750 K, 300 atm) and an inexpensive (and relatively low-activity) iron oxide catalyst (red mud) in a liquid (sump) phase reactor. The recycle solvent was a distillate from gas phase hydrogenation of the sump-phase reactor overheads. Although this technology anticipated the dispersed catalysts under development today, the process employed a high reaction severity, rather than seeking to minimize reaction severity by improved catalyst or solvent activity.

CONSOL SYNTHETIC FUELS PROCESS

In the 1960s, Consolidation Coal Company sought to improve on the performance of the German liquefaction technology by utilizing more active supported-metal hydrogenation catalysts in fixed bed reactors. To overcome catalyst deactivation problems, the coal dissolution and catalytic conversion steps of the two-stage CONSOL Synthetic Fuels (CSF) process[2] were separated by an interstage deashing step. The coal dissolution step was non-catalytic, and carried out at a relatively low temperature to produce an "extract" suitable for catalytic upgrading. The process was designed to produce a distillate hydrogen donor solvent in the second stage.[3] The role of recycle solvent was explored in bench-scale tests supported by field ionization mass

spectrometric (FIMS) and ^{1}H- and ^{13}C- nuclear magnetic resonance (NMR) analysis of the recycle solvent.[4] This work showed that, although the recycle oil increased in molecular weight upon recycle, it became less aromatic (Table 1). Recycle oil characterization was used to indicate the approach of the process operation to steady state, and revealed the important effect of solvent characteristics on other process operations, particularly solids separation.

SOLVENT REFINED COAL PROCESS

In the mid-1970s, interest grew in the development of a process to convert coal into a fuel-oil substitute for use in oil-fired electric utility boilers. The Solvent Refined Coal (SRC) process was piloted by Gulf at Ft. Lewis, WA,[5] and by Southern Company Services (and later EPRI) at Wilsonville, AL.[6] The objective of the process was to solubilize coal under hydrogen, but in a non-catalytic reaction, so that the ash-forming minerals, including pyrite, could be removed by physical means. Some organic sulfur removal also was expected. The deashed products were distilled to yield the SRC product and a distillate recycle solvent. One objective was to produce only enough distillate to remain in solvent balance. This would ensure the maximum yield of the desired SRC product, while minimizing hydrogen consumption.

Because the SRC process was designed as a thermal distillate-recycle process (perhaps aided by the catalytic effect of the coal minerals), the operating conditions had to be chosen to achieve satisfactory coal conversion, SRC yield, and desulfurization, while maintaining an adequate yield of recycle solvent. In practice, this proved to be a difficult balance to achieve. Higher reaction temperature tended to improve coal conversion and reduce SRC sulfur, but increased gas make at the expense of recycle solvent and SRC yield.[7]

In addition, because the distillate yield in the SCR process was low (typically, less then 5 wt % MAF coal), the replacement rate of the recycle solvent was low, and changes in solvent composition over time were difficult to assess. In 1977 and 1978, we obtained three relatively large and representative samples of the recycle distillate from the 6 TPD Wilsonville pilot plant for use in bench-scale liquefaction research. Some of the solvents were catalytically hydrogenated in a bench scale unit. These samples were the basis for an extensive characterization effort,[8] which included ^{1}H-NMR and ^{19}F-NMR (for determination of phenolics following derivatization), GC/MS, FIMS, reverse phase liquid chromatography, and empirical tests of solvent quality.

As the distillate recycle solvent in the SRC-I process evolved (Tables 2 and 3), it increased in total hydrogen content, but was lower in molecular weight, more aliphatic, and more phenolic. The practical consequence, as indicated by the microautoclave solvent quality tests, was that it lost hydrogen donating ability. The underlying structural changes were revealed by the NMR and FIMS data. The overall decrease in aromaticity was totally at the expense of the condensed aromatic structures; uncondensed aromatic hydrogen actually increased. The increase in aliphatic hydrogen appeared in both cyclic and aliphatic regions initially, but as the solvent further evolved, the cyclic aliphatic hydrogen decreased. The apparent loss of hydrogen donor activity under kinetic control (kinetic or KIN test) was associated with the decrease in condensed aromatic hydrogen. The decrease in conversions at the donor-limited Equilibrium or EQ conditions, designed to measure donor hydrogen content, was associated with the ratio of cyclic to alkyl aliphatic hydrogen. FIMS analysis (Figures 1 and 2) showed that

catalytic hydrogenation of the more aromatic solvent (8/77 sample) converted aromatics to hydroaromatics and improved solvent quality. Although solvent evolution increased hydrogen content (and alkyl tetralins) by an amount similar to catalytic hydrogenation, it decreased the concentration the three- and four-ring condensed aromatics and the corresponding hydroaromatics.

SELECTIVE RECYCLE AS AN IMPROVED LIQUEFACTION OPTION

The research on the evolution of the SRC distillate solvent clearly indicated the importance of higher molecular weight hydroaromatics as hydrogen donor solvent components. However, the low distillate yield in the SRC process provided few options for improving the situation, leading to the conclusion that recycle of vacuum bottoms, or a vacuum-bottoms component, would be necessary to maintain solvent quality.[8] This concept was tested by separating the SRC into "light" and "heavy" components and using the light SRC (LSRC) as a component of the recycle solvent in bench scale and microautoclave liquefaction experiments.[9] In the microautoclave experiments, the LSRC added to a Wilsonville solvent sample improved solvent quality at the "Kinetic" conditions (Table 4), but decreased conversion at the "Equilibrium" conditions indicating that it contained active hydrogen donors, but not in large concentration. The improvement seen at the EQ conditions under hydrogen pressure was surprising and the degree of improvement was remarkable. These results clearly indicated that this non-distillate oil was capable of facilitating gas phase hydrogen utilization for coal conversion in the absence of an added catalyst.

THE ROLE OF PARAFFINS IN SOLVENT QUALITY

Not all solvent quality effects can be ascribed to the activity and concentration of hydrogen donors. There has been a tendency to think in terms of "average" structures in describing coal and coal products. However, coal liquids are much more heterogeneous than an average structure might suggest. One feature of solvent quality that the FIMS data failed to reveal was the concentration of straight-chain and branched paraffinic components in recycle oils; FIMS is relatively insensitive to paraffins. In one case, the recycle distillate from a Wilsonville integrated two-stage liquefaction (ITSL) run with subbituminous coal produced a 47% wax yield upon ketone dewaxing; 12 wt % of the recycle distillate consisted of n-paraffins.[10] Simple physical removal of this wax fraction increased the solvent quality in the EQ microautoclave test from 71% to 87%.

SINGLE STAGE CATALYTIC LIQUEFACTION

The H-Coal process employs a single ebullated-bed reactor to convert coal to distillate products. In PDU and pilot plant development, a relatively high reaction temperature (825-840 °F) and resid recycle were used to achieve high conversion while minimizing reactor residence size. Compared to the SRC process, H-Coal approached a steady state recycle composition quickly[11] because of the higher turnover rate of the recycle oil components. The process solvent increased in aromaticity and phenolic -OH content with run time, corresponding to catalyst deactivation.

INTEGRATED TWO-STAGE LIQUEFACTION

The idea of separating the coal dissolution and catalytic upgrading functions was further evaluated in the development of the Lummus Integrated Two-Stage Liquefaction Process. The Lummus ITSL process used a short-residence-time (SRT), high temperature (850 °F) coal conversion stage, followed by anti-solvent deashing. The deashed oil was converted to liquid products in an

expanded-bed catalytic reactor (LC-Finer), which was operated at a lower temperature (720-750 °F) than the H-Coal reactor. The recycle oil from the second stage contained distillate and unconverted resid. Because of the thermal first stage, solvent quality was an important factor in process performance. The reactor configuration also provided an opportunity to investigate the separate roles of catalytic and thermal reactions in direct liquefaction. Comparison of the process oil characteristics in the Lummus ITSL process to those from single-stage H-Coal process were particularly instructive.[12] The results showed that hydrogen donor solvent quality was a key to coal conversion in the SRT first stage, and promoted thermal resid conversion in both stages. The lower temperature of the LC-Finer, compared to that of the H-Coal reactor, produced a more highly hydrogenated resid that, upon recycle, underwent considerable thermal conversion in the short-residence-time, high temperature first stage. The temperature of the LC-Finer also contributed to the maintenance of distillate solvent quality by minimizing cracking and isomerization reactions that could remove hydro-aromatics and their precursors (Table 5).

When the ITSL process was applied to subbituminous coals, despite the good solvent quality, coal conversion was kinetically limited, necessitating the use of a longer residence time in the first stage reactor. Extensive further development work was done on the two-stage process at the Wilsonville pilot plant, in a wide variety of configurations.[13] The Wilsonville operators concluded that it was necessary to use a dispersed iron oxide catalyst to achieve satisfactory conversion with subbituminous coal. Essentially all of the work with bituminous coals was done with two ebullated-bed catalytic reactors in series. Moderate reactor temperatures, low space velocities, and high catalyst replacement rates (relative to H-Coal), and close-coupling of reactor stages (i.e., no interstage deashing) resulted in improved yields, product quality, and selectivity. The use of a critical solvent deasher (ROSE-SR) unit allowed considerable flexibility in controlling recycle composition. The plant employed high recycle rates of heavy distillate (>750 °F IBP), resid, and unconverted coal to reduce the required per-pass conversion level. The result of these changes was a departure from the original two-stage concept of separating thermal coal dissolution and resid upgrading. Most of the feed to the first stage was recycled resid. Subsequent work has shown that the insoluble organic matter (IOM) in the recycle resid from Wilsonville is reactive for further conversion. Methods to improve solvent quality by dewaxing and hydrogenation are being evaluated.[14] This work will provide the opportunity to better define the role of recycle solvent quality in the current generation of two stage catalytic liquefaction processes.

CONCLUSIONS

In the earlier U.S. work on direct liquefaction, the goal of separating the thermal coal dissolution and catalytic distillate production steps led to process configurations that relied on hydrogen donor solvents for coal conversion. Distillate recycle solvents which evolved under mostly thermal conditions were poor hydrogen donors, but selective recycle of higher molecular weight components improved both donor content and activity. When it was realized that interstage deashing had little practical benefit, conversion of the coal in a catalytic first stage diminished the perceived need for an active hydrogen donor solvent. For subbituminous coals, donor solvent hydrogen alone did not appear to be adequate to achieve satisfactory conversions, leading to the use of dispersed catalysts, greater reaction severity, and solids recycle. However, the improvements of two-stage liquefaction came at the expense of reduced space velocity and increased catalyst usage. Current research is looking to replace the supported-

catalyst systems with dispersed catalysts that offer higher selectivity and activity, while avoiding the capital cost of a supported-catalyst system. As this research and development continues, it will be important to understand and evaluate the role of vehicle solvents, and to look for opportunities to utilize solvent-mediated reactions as part of a overall strategy for reducing the cost of producing liquids from coal.

ACKNOWLEDGEMENT

The work discussed in this paper was supported by the CONSOL Inc., the U.S. Department of Energy, and the Electric Power Research Institute. We are indebted to many colleagues, particularly those at CONSOL, DOE, EPRI, HRI, the Wilsonville Advanced Liquefaction Test Facility, and Lummus-Crest for their contributions to this work.

REFERENCES

1. Bergius, F., German Patent No. 301,231, August 9, 1913.
2. Gorin, E.; Kulik, C. J.; Lebowitz, H. E. *Ind. Eng. Chem. Process Des. Dev.* 1977, *16*, 95.
3. Curran, G. P.; Struck, R. T.; Gorin, E. *Ind. Eng. Chem. Process Des. Dev.* 1967, *6*, 166.
4. Kleinpeter, J. A.; Jones, D. C.; Dudt, P. J.; Burke, F. P. *Ind. Eng. Chem. Process Des. Dev.* 1979, *18*, 535.
5. Pittsburg and Midway Coal, "Solvent Refined Coal (SRC) Process, Annual Report, 1976", DOE Report FE-496-131 (May 1977).
6. Lewis, H. E.; Weber, W. H.; Usnick, G. B.; Hollenack, W. R.; Hooks, H. W. "Solvent Refined Coal (SRC) Process. Operation of Solvent Refined Coal Pilot Plant at Wilsonville, AL. Annual Technical Progress Report, January-December 1976", DOE report No. FE-2270-15 (June 1977).
7. Styles, G. A.; Weber, W. H.; Basu, A. "Short Residence Time Studies Utilizing the Dissolver Preheater at the Wilsonville SRC Pilot Plant", Proceedings, EPRI Contractor's Conference on Coal Liquefaction, Palo Alto, CA, May 1978.
8. Burke, F. P.; Winschel, R. A.; Pochapsky, T. C. "Composition and Performance of Distillate Recycle Solvents from the SRC-I Process", *Fuel* 1981, *60*, 563.
9. Kleinpeter, J. A.; Burke, F. P. "Conventional and Short Residence Time Coal Liquefaction Using Selective Product Recycle", Proceedings, EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, CA, May 1979.
10. Winschel, R. A.; Robbins, G. A.; Burke, F. P. "Improvement in Coal Liquefaction Solvent Quality by Dewaxing", *Fuel* 1987, *66*, 654.
11. Burke, F. P.; Winschel, R. A. "Slurry Recycle Oil Composition and Process Performance in H-Coal PDU Operations", Proceedings, Sixth Annual EPRI Contractors' Conference, Palo Alto, CA, May 1981.
12. Winschel, R. A.; Burke, F. P. "Process and Product Oil Characterization in Two-Stage Coal Liquefaction", Proceedings, Eighth Annual EPRI Contractors' Conference on Coal Liquefaction, Palo Alto, CA, May 1983.
13. Lee, J. M.; Vimalchand, P.; Cantrell, C. E.; Davies, O. L. "Major Accomplishments at the Advanced Coal Liquefaction Test Facility at Wilsonville", DOE Liquefaction Contractors' Review Conference, Pittsburgh, PA, September 1992.
14. Derbyshire, F. J. "Improved Coal Liquefaction through Enhanced Recycle Distillate Quality", Proceedings, DOE Coal Liquefaction Contractors' Conference, September 1993.

Table 1. Proton Distributions of Recycle Solvents in the CSF Process

	H–Distributions, Normalized			
	Aromatic	Alpha	Beta	Gamma
Cycle 1	50	39	9	2
Cycle 2	49	35	12	3
Cycle 3	43	37	16	4
Cycle 4	40	37	18	6

Table 2. Characterization of Recycle Solvents from Wilsonville SRC–I Operations

	Hydrogen, wt%						Solvent Quality	
Sample		Aromatic		Aliphatic		–OH,	KIN	EQ
Date	Total	Condensed	Uncond	Cyclic	Alkyl	meq/g		
8/77	8.0	2.15	0.90	1.96	2.99	1.23	81.4	76.5
4/78	9.0	1.31	0.95	2.29	4.45	1.51	76.5	74.4
10/78	8.9	1.21	1.09	1.99	4.61	1.66	75.4	67.4
Hydro (8/77)	8.9	1.89	0.83	2.54	3.64	0.68	80.9	85.6

Table 3. Comparison of Wilsonville Solvents by FIMS

	Differences, mol % of total liquid	
	Batch VI – Batch I	Hydro – Batch I
Naphthalene	–0.9	–2.1
Tetralin/Indans	4.8	3.1
Mass 178	–3.1	–1.5
Hydro Mass 178	–1.9	2
Mass 202	–1.1	–0.6
Hydro Mass 202	–0.7	1.3
Carbazole	–0.1	
Quinolines		–1.1
Hydroquinolines		0.3
Indanols	1.3	–1.4
Phenols	5.9	–0.2

Table 4. Effect of Kerr–McGee Light SRC addtion on Wilsonville solvent quality (4/78 sample)

LSRC	H2	Solvent Quality	
wt%	psig cold	KIN	EQ
0	0	76.5	74.4
25	0	79.1	73.7
50	0	88.6	65.5
25	1000	85.6	82.8
50	1000	87.6	86.2

Table 5. Comparison of Lummus ITSL (Run 2SCT9) and H–Coal (PDU Run 9) Recycle Distillates

	Concentration, wt%	
	ITSL	H–Coal
Aromatics	12	8
n–Alkyl Aromatics	10	20
Hydroaromatics	31	8
Cyclo–Penta Arom	6	18
n–Alkanes	1	6

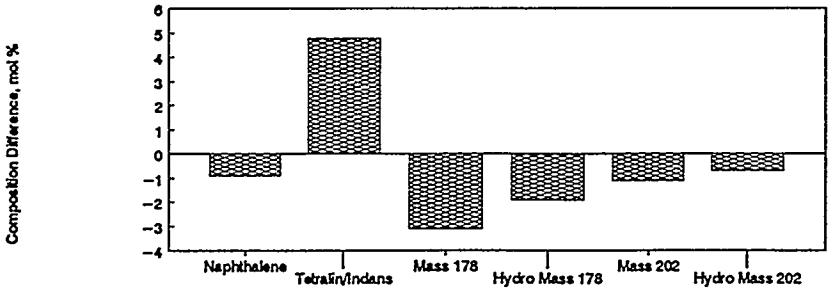

Figure 1. FIMS Comparison: Batch VI–Batch I.

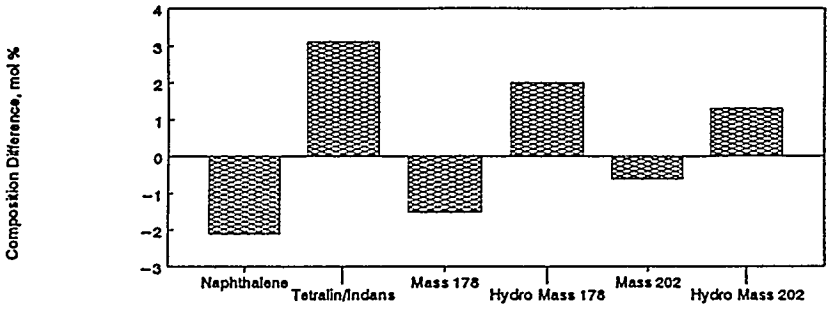

Figure 2. FIMS Comparison: Hydro I–Batch I.